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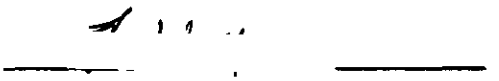

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GRIGNARD COMPOUNDS. COMPOSITIONS AND MECHANISMS OF REACTION

A THESIS

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SUMMARY

PART I. COMPOSITION IN TRIETHYLAMINE. TERTIARY AMINES AS COMPLEXING AGENTS FOR COMPOSITION STUDIES

The composition of Grignard compounds in tertiary amine solvent was established by fractional crystallization and redistribution studies. The composition was shown to be best represented by the equilibrium $R_2Mg + MgX_2 \rightleftarrows 2RMgX$. This equilibrium was found to lie almost completely to the right when X = Br and, based on the generally similar results obtained when the chloride and bromide systems were fractionally crystallized, the equilibrium is also thought to lie far to the right when X = Cl. The equilibrium is not nearly so much to the right when X = I. The triethylamine complexes of R_2Mg and MgX_2 that were studied, redistribute in triethylamine and the tetramethylethylenediamine complexes that were studied, redistribute in both diethyl ether and benzene. The triethylenediamine complexes that were examined are insoluble in diethyl ether, benzene and n-hexane. For these reasons, none of these amines are suitable complexing agents for establishing the equilibrium composition of Grignard compounds.

PART II. NATURE OF THE ASSOCIATION IN TETRAHYDROFURAN AND DIETHYL ETHER

Ebullioscopic data are presented for tetrahydrofuran and diethyl ether solutions of several Grignard and related magnesium compounds over

a wide concentration range. Analysis of the data is accomplished by observing the change in association (i) with concentration and by consideration of the constancy of the equilibrium constants calculated for several possible descriptions of the associated system. The expected nonideality of the solutions studied was considered in the interpretation of the data. While all of the compounds studied were found to be monomeric in tetrahydrofuran, the alkyl- and arylmagnesium bromide and iodides were found to be monomeric in diethyl ether only at low concentration, (<0.1 M) while exhibiting in general an increase in association with concentration. Interpretation of the data indicates that these compounds are associated in a polymeric fashion. In contrast the alkylmagnesium chlorides in diethyl ether associate to form stable dimers with the association insensitive to concentration changes. Comparison of the data for magnesium halides and dialkylmagnesium compounds in diethyl ether indicates that, except for the methyl compound, association is considerably stronger for the magnesium halides than for the dialkylmagnesium compounds. Thus, except for the methylmagnesium halides, Grignard compounds associated with bridging mainly through the halogen atom. The methylmagnesium halides are exceptional since methyl bridging is strong enough in diethyl ether to permit association by bridging through either the methyl group or the halogen atom. Although the steric requirements of the alkyl group has some effect on the association of Grignard compounds, the effect is generally small compared to the effect of halogen or solvent.

PART III. REACTION OF METHYLMAGNESIUM BROMIDE WITH BENZOPHENONE IN DIETHYL ETHER. MECHANISMS AND PRODUCTS

The reaction of methylmagnesium bromide with benzophenone in diethyl ether results in the formation of not only the addition product (1,1-diphenylethanol) but also a significant quantity of side products, one of which has been tentatively identified as benzopinacol. These results cast doubt on all of the mechanisms proposed thus far for the addition reaction because the contribution by the side reaction to the disappearance of ketone has not received adequate consideration. Unfortunately, the side reaction caused such analytical difficulties that no conclusions about the mechanism of the addition reaction could be reached.

PART I

COMPOSITION IN TRIETHYLAMINE. TERTIARY AMINES AS COMPLEXING AGENTS FOR COMPOSITION STUDIES

CHAPTER I

INTRODUCTION

Background

The preparation of Grignard reagents in ether solvents and the reaction of these compounds with various organic functional groups have been known to chemists for decades. However, it is only recently that the composition of this highly useful reagent has been demonstrated. The controversy surrounding the composition problem, coupled with the reagent's popularity for organic syntheses, have resulted in the accumulation of a great deal of data concerning directly or indirectly, the Grignard reagent in ether solvents (1,2,3,4).

Preparation and Reaction of Grignard Compounds in Tertiary Amine Solvents

Recent effort has been directed towards the discovery of new solvents, particularly nitrogen-containing solvents, that might function in place of ethers for the preparation and reaction of Grignard compounds; hexamethylphosphoramide (5,6,7) and disubstituted amides (6) have been investigated for this purpose. Surprisingly, little effort has been directed towards the use of pure amine solvents for Grignard compounds (8) although tertiary amines, substituted amides and nitrogen heterocycles have been used in stoichiometric amounts for the preparation and/or reaction in ether (9,10) and hydrocarbon (11,12) diluents. Some reactions in nitrogen-containing solvents have been studied with Grignard com-

pounds prepared in diethyl ether which was subsequently displaced with the secondary solvent (13). Recently the direct preparation and reaction of Grignard compounds in triethylamine was accomplished for the first time (14).

Composition of Grignard Compounds in Tertiary Amine Solvents

There is little information available about the composition of Grignard compounds when prepared directly in amine solution. Ethylmagnesium bromide in diethyl ether was treated with triethylamine and the resulting ethylmagnesium bromide triethylaminate was then crystallized for a structural study (15). The only other composition study (16) involved the fractional crystallization of the solution resulting from the reaction between ethyl bromide and magnesium in triethylamine.

Tertiary Amines as Complexing Agents for the Determination of the Composition of Grignard Compounds

The information available is very limited. The only report suggested that triethylamine functioned satisfactorily (16) as a complexing agent for the determination of the composition of ethylmagnesium bromide in diethyl ether. A report on a related system suggested that tetramethylethylenediamine (TMED) was used (17) successfully as a complexing agent in the study of the composition of the zinc analog of the Grignard reagents.

Purpose

This study was undertaken to establish the composition of the Grignard reagent in triethylamine, the nitrogen analog of diethyl ehter,

and to explore the feasibility of using a tertiary amine as a complexing agent for composition studies in other solvents.

CHAPTER II

EXPERIMENTAL

Instrumentation and Apparatus

The magnesium halide hydrolysates were examined on a dual column gas chromatograph (F&M Scientific Model 750) using columns packed with Polypak 2 (F&M Scientific).

The nmr spectra of the Grignard and redistribution solutions were obtained on a Varian A-60 spectrometer.

The inert atmosphere box was manufactured by Kewaunee (Model 2C1020) and was equipped with a recirculating system (18) to continually remove oxygen and water contaminants from the nitrogen atmosphere.

The syringes which were used for sample transfer in the redistribution studies were equipped with stainless steel needles.

The remainder of the equipment was standard laboratory glassware unless a modification is specified in an individual experiment.

Chemicals

Bromine (Matheson Reagent), iodine (Baker Analyzed), and dialkylmercury compounds (Metallomer) were used without further purification.

The alkyl and aryl halides (Reagent Grade from Eastman), after drying over Na_2CO_3, were distilled under dry nitrogen through a 1.5 foot column packed with glass helices.

Triethylamine (Eastman Reagent), TMED (Eastman Reagent), THF (Fisher Certified), benzene (Baker Thiophene-Free), and hexane (Fisher

Certified) were distilled from $NaAlH_4$ through a two foot Vigreaux column under dry nitrogen just prior to use. Anhydrous diethyl ether (Fisher Certified) was distilled in a similar manner from $LiAlH_4$. Triethylenediamine (Houdry) was dried by boiling with anhydrous benzene and using a Dean-Stark head to collect the water-benzene azeotrope.

Grignard grade magnesium (Fisher Reagent) was used to prepare the Grignard compounds used in the fractional crystallization studies. Triply sublimed magnesium (Dow) was employed in the preparation of the compounds used in the redistribution studies. In the preparation of all of the compounds, the magnesium was placed into the apparatus for drying.

All manipulations of the chemicals were carried out either in a glove box (dry nitrogen atmosphere) or on the bench top in sealed systems under dry nitrogen. All equipment that came in contact with the chemicals was dried by flash flaming under vacuum or under a flow of dry nitrogen.

Analyses

The analysis for magnesium was accomplished by titration with EDTA (Eriochrome Black-T indicator), and halide analyses were completed by titration with silver nitrate (potentiometrically or Volhard). Analysis for nitrogen was carried out by adding an aliquot of standard acid to the sample and then back-titrating with NaOH solution (phenolphthalein indicator). The difference between the acid consumed and the total Mg content (by EDTA) indicated the amount of complexed amine. However, the alkylmagnesium iodides gave uninterpretable results since the first fractions gave either a very small value or a negative number for the nitro-

gen content. In contrast, the latter fractions gave very large values. A reasonable explanation for these results rests with the conclusions drawn about the composition of the alkylmagnesium iodide fractions from the Mg:halogen ratios. Thus, since the first fraction contains mainly MgI_2 and very little of any material with an active carbon-magnesium bond, the relatively small amount of acid consumed is due mainly to the complexed triethylamine. When the value for the Mg content is subtracted, a very small value or negative number results for the nitrogen content. The later fractions, composed mainly of R_2Mg, require a large amount of acid and subtraction of the total Mg content results in a value suggesting an unreasonably large amount of triethylamine complexed with the magnesium compound.

Preparations and Procedures

Preparation of Grignard Reagents in Triethylamine.

The methods used for the preparation of Grignard compounds in triethylamine are very similar to those used for the preparation in ethers. The only additional precaution that must be observed is that the alkyl halide should not be in contact with the solvent any longer than is necessary, especially in the cases where the alkyl halide is prone to quaternary salt formation and/or dehydrohalogenation. The preparation of ethylmagnesium bromide is typical of the methods employed. Two addition funnels, one with ethyl bromide (54.5 g, 0.5 mol) and one with triethylamine (400.0 ml), were placed on opposite sides of a one-liter three-necked flask containing magnesium (36.4 g, 1.5 g-atom). The funnel containing triethylamine shared a Claissen adapter with a water-cooled con-

denser; the funnel with the alkyl halides was connected directly to the flask so that the liquid dropped directly into the reaction mixture. After adding 50 ml triethylamine to the magnesium, the reaction was initiated by adding 5 ml ethyl bromide. After the reaction began, as evidenced by a spontaneous evolution of heat, stirring (motor assembly with an oil-sealed bearing) was started and the addition rates of solvent and halide were adjusted to maintain a reaction temp. of 45-50°. A precipitate formed at the very beginning of the reaction and the quantity increased throughout the addition step. When addition was complete, the stirring was continued for 12 hr while maintaining a temp. of 50° with external heating.

Fractional Crystallization of Grignard Reagents Prepared in Triethylamine

The crystallization results reported in Table 2 were obtained in the following manner. The solid-liquid mixture formed in the Grignard preparation reactions was separated by filtration. The solid material was separated from the excess magnesium used in the reactions by solution of the Grignard component in benzene, followed by filtration of the magnesium. The benzene filtrate was then subjected to vacuum distillation in order to produce the solid that was labeled fraction 1. The other fractions were obtained by slow removal of the triethylamine solvent from the original filtrate under vacuum until crystallization had begun. In this way usually several fractions were isolated. The last fraction was always the residue obtained after complete removal of the triethylamine solvent under vacuum.

Preparation of Grignard Reagents in Diethyl Ether

The preparation of n-butylmagnesium iodide will illustrate the

method employed. Two addition funnels, one with 1-iodobutane (2.0 mol, 268.1 g) and one with diethyl ether (900.0 ml), were connected to a one-liter three-necked flask containing magnesium (2.2 g-atom, 53.5 g). After initiating the reaction by adding 50 ml ether and 5 ml 1-iodobutane, stirring (motor assembly with an oil-sealed bearing), was started. The ether and the halide were added simultaneously at a rate to maintain gentle boiling as evidenced by a slow solvent return from the tip of the Dry Ice condenser. After stirring overnight at room temperature, the solution was filtered through a glass wool plug to remove unreacted magnesium.

Fractional Crystallization of Ethereal Grignard Reagents from Triethylamine

This operation will be illustrated with n-butylmagnesium iodide. An addition funnel containing the Grignard compound in ether (50.0 ml., 89.0 mmol) was connected to a one-liter three-necked flask equipped with a stirring assembly (oil-sealed bearing) and a water-cooled condenser. Triethylamine (500.0 ml) was stirred rapidly while the Grignard was dripped slowly into the flask at room temperature. After stirring overnight the solution was fractionally crystallized by slowly removing the triethylamine under vacuum at room temperature. The fractions were dried for three days on a vacuum manifold.

Preparation of Dialkylmagnesium Compounds

To a 200 ml round-bottom flask containing 10.6 g (0.43 g-atom) triply sublimed Mg, was added 50.0 g (0.22 mol) dimethylmercury. The flask was connected to a water-cooled condenser and the contents mixed with a magnetic stirrer at room temp. The reaction started within 15 minutes as evidenced by heat release and formation of a white solid ac-

companied by the appearance of free mercury in the flask. Stirring was continued for two days. The flask was then transferred to a small distillation unit. The receiver was cooled by Dry Ice-acetone and the system was evacuated overnight to remove any unreacted dimethylmercury. The procedure for the preparation of diethylmagnesium from diethylmercury, was similar except that the reaction mixture was heated with an oil-bath to 65-70° during the reaction.

Solutions of the magnesium alkyl in triethylamine and diethyl ether were prepared by adding a sufficient quantity of the solvent directly to the flask to dissolve the solid. Dimethylmagnesium TMED was prepared by adding the amine (14.5 g, 0.125 mol) to an ether solution of dimethylmagnesium (0.056 mol); a portion of the solution was removed via syringe for the redistribution studies in diethyl ether. The remainder was isolated and dried under vacuum for the study in benzene.

Dimethylmagnesium triethylenediaminate was prepared by mixing diethyl ether solutions of dimethylmagnesium (0.029 mol) and triethylenediamine (0.065 mol). The resulting precipitate, which did not dissolve in excess ether, was isolated and mixed with benzene and hexane; the complete lack of solubility in either solvent was demonstrated by the absence of any reaction when the liquid portion was removed and treated with water. Diethylmagnesium triethylenediaminate was prepared in the same manner as the methyl complex.

Preparation of Magnesium Halides

Triply sublimed magnesium (24.3 g, 1.0 g-atom) was placed in a 500 ml round-bottom flask containing a large stirring bar. The flask was connected via two Claissen adapters to a water-cooled condenser, an

addition funnel containing 79.9 g (0.5 mol) bromine and an addition funnel containing 500 ml diethyl ether. Initially, 75 ml ether was added to the magnesium and cooled with an ice bath. A few drops of bromine were added to the cooled ether-magnesium mixture, decolorization was immediate. The ether and bromine were added simultaneously while the reaction was moderated with the ice bath. After filtering to remove the unreacted magnesium, the reaction product was recrystallized from ether four times to yield white magnesium bromide etherate. A glpc analysis of a portion of the hydrolyzed material revealed no impurities in the organic layer.

A 500 ml round-bottom flask containing 19.4 g (0.8 g-atom)triply sublimed magnesium and a stirring bar was connected via a Claissen adapter to an addition funnel filled with 101.5 g (0.4 mol) iodine in 450 ml diethyl ether and to a water-cooled condenser. After the small initial addition had decolorized the iodine solution was added to the stirred magnesium at a rate to maintain gentle boiling of the ether. After filtering to remove unreacted magnesium, the reaction product was recrystallized three times from ether to yield white magnesium iodide etherate. A glpc analysis detected no impurities in the hydrolyzed material.

Ether was displaced from magnesium bromide with triethylamine by dissolving a portion of the magnesium bromide etherate (27.1 g, 0.10 mol) in a minimum of diethyl ether in a 200 ml round-bottom flask. The flask was connected to a Claissen adapter fitted with an addition funnel containing 350 ml triethylamine and a distillation unit with a five cm distilling column packed with glass helices. The ether solution was heated

to boiling while being mixed by a magnetic stirrer. When the ether started to distill, the triethylamine was introduced at a rate to maintain a constant volume of solution in the distilling flask. Addition of the triethylamine was continued until the temperature of the distillate remained constant. The remainder of the solvent was removed by distillation and by drying the solid product on a vacuum manifold overnight. A portion of the tan powder was hydrolyzed and glpc analysis revealed that displacement of the ether was complete. Anal. Calcd for $MgBr_2 \cdot NEt_3$: Mg, 8.52; Br, 56.02; Mg:Br, 1.00:2.00. Found: Mg, 8.16; Br, 53.42; Mg:Br, 1.00:1.99. The same treatment of the magnesium iodide etherate followed by a glpc analysis of the hydrolysate indicated that 99.6+% of the ether had been replaced by triethylamine. Anal. Calcd for $MgI_2 \cdot NEt_3$: Mg, 6.41; I, 66.91: Mg:I, 1.00:2.00. Found: Mg, 6.29; I, 66.44; Mg:I, 1.00:2.02.

Magnesium bromide TMED was prepared by adding the amine (5.1 g, 0.044 mol) via syringe to an ether solution of the halide (0.022 mol) and was not isolated for the redistribution study with dimethylmagnesium TMED in diethyl ether. A second sample of the compound was prepared in the same manner but was isolated and dried under vacuum for the exchange study in benzene.

The magnesium bromide triethylenediaminate complex was prepared by treating a diethyl ether solution of magnesium bromide (0.023 mol) with triethylenediamine (0.056 mol) dissolved in diethyl ether.

Redistribution Studies

The apparatus and procedure employed was the same for all of the redistribution studies. A 500 ml round-bottom flask was equipped with

a septum cap opening for addition and withdrawal of samples by syringe. The nitrogen was supplied through the top of a water-cooled condenser and the reaction mixture was mixed by a stirring bar. Prior to addition of the magnesium alkyl solution, the amount of magnesium halide dissolved in the pure solvent was determined by analyzing for magnesium and halogen. This gave the value for the initial halogen concentration and the value for magnesium, when added to that calculated for the magnesium alkyl, gave the initial magnesium concentration. After addition of the magnesium alkyl solution, samples were withdrawn periodically for analysis.

Thus, a magnesium bromide triethylaminate (0.019 mol)-triethylamine mixture was treated with a triethylamine solution of dimethylmagnesium triethylaminate (0.019). Similarly, a triethylamine solution of diethylmagnesium triethylaminate (0.022 mol) was added to a triethylamine-magnesium bromide triethylaminate (0.021 mol) mixture and diethylmagnesium triethylaminate (0.020 mol) in triethylamine was added to magnesium iodide triethylaminate (0.020 mol) in triethylamine. Redistribution of dimethylmagnesium TMED and magnesium bromide TMED in diethyl ether was examined by adding 100% excess of TMED to ether solutions of the compounds and then mixing the solution of dimethylmagnesium (0.019 mol) with the magnesium bromide (0.022 mol)-ether mixture. The exchange study in benzene was conducted by adding a benzene solution of dimethylmagnesium TMED (0.019 mol) to a mixture of magnesium bromide TMED (0.020 mol) in benzene.

NMR Analysis of the Grignard Compounds and Redistribution Products in Triethylamine.

The nmr tubes were filled in the dry box via syringe with a solu-

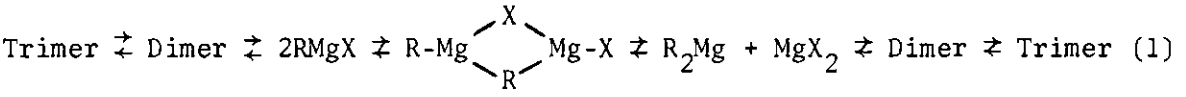
tion of dimethylmagnesium, a mixture of dimethylmagnesium-magnesium bromide and a solution of methylmagnesium bromide prepared from methyl bromide and magnesium in triethylamine. After filling, the tubes were sealed with tightly fitting plastic caps and the spectra were run immediately at room temperature. Corresponding samples for the ethylmagnesium bromide and iodide systems were prepared and examined in the same amnner.

CHAPTER III

RESULTS AND DISCUSSION

Redistribution of Magnesium Alkyls and Magnesium Halides in Triethylamine

Several factors must be considered before discussing the composition of Grignard compounds in triethylamine. In ether solvents the Grignard compound is actually a system of equilibria with the interconversion of A to C (Eq. 1) thought to occur via intermediate B (1,19).



It is also known that Grignard reagents exist in diethyl ether as molecular aggregates with the degree of association dependent on the concentration; however in tetrahydrofuran the compounds are predominanaly monomeric (20,21,22). This difference in association results from a stronger coordination of the magnesium atom by tetrahydrofuran than by diethyl ether which prevents the formation of an appreciable concentration of bridged compounds. Since triethylamine is also a good Lewis base toward certain Lewis acids, coordination with the magnesium atom might be strong enough to completely stop the formation of bridged compounds such as B. Since this would eliminate any interconversion of A and C, the Grignard in triethylamine would be composed of the initial species formed

when an alkyl halide reacts with magnesium in this solvent.

The relative insolubility of magnesium halides* and the solubility of magnesium alkyls in triethylamine offer a convenient method for studying the interconversion of A and C. If the magnesium halide and dialkylmagnesium are mixed in triethylamine, the formation of A can be determined by following the change in magnesium and halogen content of the solution.

Results from molecular weight studies in amines (16,23,24) and THF (20,21,22) show that magnesium compounds are monomers in solution when complexed with a solvent that is a stronger Lewis base than diethyl ether. Therefore, an increase in the magnesium and halogen content of the solution cannot be attributed to some type of association or ion-pairing phenomena which would result in the formation of dimers or other associated forms in solution but must be indicative of redistribution to form the monomeric RMgX compound. Thus, when diethylmagnesium triethylaminate was combined with either magnesium bromide triethylaminate or magnesium iodide triethylaminate in triethylamine, redistribtuion occurred (Table 1) to form the soluble ethylmagnesium bromide and partially soluble ethylmagnesium iodide, respectively.

The decrease in solubility observed when dimethylmagnesium triethylaminate and magnesium bromide triethylaminate were mixed in triethylamine (Table 1) is a little more difficult to interpret due to a report (15) that the addition of triethylamine to an ethereal solution

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*This is known for magnesium bromide and iodide but not for magnesium chloride. It has been assumed that magnesium chloride would also be only sparingly soluble in triethylamine.

of ethylmagnesium bromide produces, upon crystallization, solid material with the formula $(EtMgBr)_2(Et_3N)_2$. Dimer formation in the solid was attributed to a steric preference for the interaction of the magnesium atom with a triethylamine molecule and a bromine atom to that with two triethylamine molecules to form a disolvated monomer. The possibility exists, therefore, that the decrease in solubility in the methyl system is due to the precipitation of a dimethylmagnesium-magnesium bromide complex rather than the precipitation of methylmagnesium bromide formed by redistribution.* However, there is no reason to believe that the methyl system would not be at least as prone to redistribution as the ethyl system. Certainly any requirement to form an intermediate with alkyl bridges (B, Eq. 1) should be met with ease by the methyl system due to the good bridging properties of the methyl group (22,25).

Earlier it was reported (16) that diethylmagnesium triethylaminate and magnesium bromide triethylaminate did not exchange in triethylamine solvent. The magnesium bromide used in this experiment was prepared by the familiar method (26,27,28) which involves the reaction of magnesium metal and bromine in diethyl ether. Since then it has been found that this method produces an impure product when prepared according to the

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*Although the diethylmagnesium-magnesium iodide system also precipitated some material, this presented no problem in interpreting the results since the magnesium content of the solution was greater than that due solely to the solubility of magnesium iodide and diethylmagnesium. The overall result, then, was a substantial increase in the magnesium and iodine content of the solution which can be attributed only to the formation of EtMgI. In the methyl system, the solution has a magnesium and bromine analysis only a little greater than found for dissolved magnesium bromide and therefore prevents an easy interpretation of the results.

literature method although Mg:Br ratio of the product is 1:2. Unfortunately the determination of the Mg:Br ratio of the product in solution turned out to be a deceptive criteria of purity. The ether is highly brominated in this reaction resulting in the production of $MgBr_2$ which is complexed to highly reactive brominated ethers. This contaminent is believed to have been at least partly responsible for the erroneous results reported earlier.* It is only on repeated fractional crystallization that the brominated ether can be removed from the product and 99+% pure $MgBr_2$ obtained (29).

Fractional Crystallization of Grignard Compounds in Triethylamine

The interconversion of A and C suggests that there is an equilibrium in triethylamine similar to that found in ethers (Eq. 1). This equilibrium can be detected by taking advantage once again of the low solubility of magnesium halides in triethylamine. As pointed out earlier, all indications are that the various magnesium compounds in triethylamine are monomers in solution. Therefore, if the Grignard is a mixture of dialkylmagnesium and magnesium halide, they will be present as monomers and fractional crystallization of the solution will cause the magnesium halide (least soluble) to precipitate in the early fractions and the dialkylmagnesium (most soluble) to precipitate in the later fractions. The first fractions then will have a magnesium to halogen ratio

*The major conclusion of the previous study (16) is still valid; namely, that the existence of RMgX species in solution has been definitely demonstrated and that this is the predominant species in triethylamine solution. However the conclusion that RMgX is the species first formed in the reaction of RX and Mg in diethyl ether and is the predominant species in diethyl ether is not necessarily true since the RMgX could have been formed by the redistribution of R_2Mg and MgX_2.

approaching one to two and the last fractions will have a magnesium to halogen ratio approaching one to zero. If all of the fractions are the same, as shown by a constant magnesium to halogen ratio of one to one, this would indicate that the equilibrium lies entirely in the direction of a single monomeric compound, i.e., the alkylmagnesium halide.

When the Grignard reagents prepared in triethylamine were fractionally crystallized (Table 2), a magnesium to halogen ratio of one to one was found in most cases except when the halogen was iodine. This can be seen by examining the data for ethylmagnesium chloride, bromide and iodide.

When the alkyl group is changed from ethyl to s-butyl, a magnesium to halogen ratio of one to one is found for all fractions for the chloride, however, the bromide shows a high halogen analysis in the first fraction. This high halogen analysis in the first fraction is not due to magnesium bromide from a di-s-butylmagnesium-magnesium bromide equilibrium since the last fraction does not show a correspondingly high magnesium analysis demanded by precipitation of di-s-butylmagnesium. The high halogen content of the first fraction could be due to dehydrohalogenation of the alkyl halide by the amine to form triethylammonium bromide, coupling of the alkylmagnesium halide with the alkyl halide to form magnesium halide, and/or quaternary ammonium salt formation from the amine and the alkyl halide.

The results from s-butylmagnesium iodide offer a convenient comparison. As with ethylmagnesium iodide but not s-butylmagnesium bromide, the high halogen analysis found in the first fractions is accompanied by a high magnesium analysis in the later fractions. The compounds t-butyl-

magnesium chloride and t-butylmagnesium bromide also displayed high halogen analysis in the first fraction without the required low halogen analysis in the final fractions. The only aromatic Grignard studied, phenylmagnesium bromide displayed an unusual analysis in some ways similar to the s-butylmagnesium bromide and t-butylmagnesium bromide and chloride. This probably results from coupling of the aromatic Grignard with bromobenzene to form magnesium bromide and biphenyl.

Somewhat similar results were observed when a series of Grignard reagents was prepared in diethyl ether and then added to triethylamine. After fractional crystallization of the triethylamine solutions, 1:1 magnesium to halogen ratios were obtained in every case (Table 3) except when the halogen was iodine. Thus, ethylmagnesium bromide, phenylmagnesium bromide, t-butylmagnesium chloride and isopropylmagnesium chloride gave, within experimental error, Mg:halogen ratios of one to one. The high halogen analyses in the first fractions that were found when phenylmagnesium bromide and t-butylmagnesium chloride were prepared by reacting the halide with magnesium directly in triethylamine (Table 2) are absent for these compounds prepared in diethyl ether and then added to triethylamine.

The only compound to give a different result was n-butylmagnesium iodide where the magnesium to iodide ratio approached one to two in the initial fraction and the last fraction displayed a high magnesium analysis. This result for n-butylmagnesium iodide compares favorably with the previously mentioned results obtained when ethylmagnesium iodide and s-butylmagnesium iodide (Table 2) were prepared directly in triethylamine.

Due to the monomeric nature of the solutions, the empirical formula

ratios obtained by analysis of the solid fractions are equivalent to the molecular formula ratios of the material in solution. Thus, in the cases where only RMgX was isolated from the Grignard-triethylamine system (when X = Cl, Br), it can be concluded that the predominant species in solution is RMgX and that the Schlenk equilibrium (Eq. 1) lies far to the right; this conclusion is supported by the redistribution studies (Table 1).* This agrees with the previously mentioned report (15) that the material obtained by adding triethylamine to an ether solution of ethylmagnesium bromide produces solid material formulated as dimeric EtMgBr. This isolation of magnesium iodide and dialkylmagnesium from the alkylmagnesium iodides must be interpreted with care. The precipitation of magnesium iodide simply indicates its presence; the amount isolated does not necessarily reflect the equilibrium concentration in solution. This is so because removal of this compound from the equilibrium system would simply result in shifting the equilibrium to regenerate more magnesium iodide.**

Thus, a large amount of magnesium iodide could be isolated by fractional crystallization although only a small quantity may be present in solution at equilibrium. This is observed when dioxane is added to

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*Formulation of the alkylmagnesium chlorides as predominantly RMgX is based on the generally similar results obtained when the chloride and bromide systems were fractionally crystallized.

**This would not be true if the interconversion of A and C is so slow that the fractionation could be completed before the equilibrium system could compensate for the material removed. The redistribution studies and other recent work (24,30) indicate that the interchange is rapid.

etheral Grignards to isolate the dialkylmagnesium compound. Although the exact position of the equilibrium cannot be stated, the fact that alkylmagnesium iodides have a much greater solubility than magnesium iodide in triethylamine suggest an appreciable concentration of RMgX in the alkylmagnesium iodide solutions.

The use of nmr would be the obvious method for determining the equilibrium composition of Grignard reagents in triethylamine. However, in the case of methylmagnesium bromide in triethylamine, any difference in the nmr spectra of methylmagnesium bromide and dimethylmagnesium solutions could not be observed due to the low solubility of the Grignard compound prepared either by redistribution of dimethylmagnesium and magnesium bromide or by a direct combination of magnesium and methyl bromide in triethylamine. Further, in the soluble ethyl system, the diethylmagnesium and ethylmagnesium bromide solutions gave spectra that were similar enough so as to prevent an easy interpretation of the results. This latter finding agrees with earlier reports (30,31,32,33,34) on similar systems in ether solvents.

Redistribution of Dimethylmagnesium and Magnesium Bromide As Tetramethylethylenediamine Complexes in Diethyl Ether and Benzene

Apparently triethylamine is not a Lewis base of sufficient strength to prevent the formation of B and thus stop the interconversion of A and C. The discovery of a complexing agent that would stop the inter conversion of A and C would allow the determination of equilibrium constants for the Grignard reagent in various solvents by simply complexing the reagent with the base and then fractionally crystallizing the

solution. Tetramethylethylenediamine (TMED) was used with success for a similar study with the zinc analog of Grignard reagents (17). The feasibility of using TMED as the complexing agent for Grignard reagents in diethyl ether was demonstrated by finding that magnesium halide TMED complexes are only slightly soluble and dialkylmagnesium TMED complexes are very soluble in diethyl ether. However, dimethylmagnesium TMED and magnesium bromide TMED redistributed in diethyl ether to form the relatively insoluble methylmagnesium bromide TMED complex (Table 4).

These findings agree with other recent reports (24,30). With alkyl exchange in dialkylmagnesium systems (30), it was found that exchange in diethyl ether-THF mixtures is retarded but not stopped by complexing agents such as TMED. The acceleration of the exchange by added magnesium bromide (30) suggests that the alkyl-halogen interchange studied here might be even more facile and therefore more difficult to stop than the alkyl-alkyl exchange.

The failure of complexing agents to prevent the interconversion of A and C raises the possibility that redistribution and disproportionation may follow a mechanism other than the one shown by Eq. 1. The presence of ions in ether solvents has been reported (35,36), so that it is reasonable to expect that the greater complexing ability of tertiary amines would stabilize and thus enhance formation of charged species in solution. An ionic mechanism can be envisioned (Eq. 2), based on the principle ions reported in ether solvents. Therefore if the compounds are first complexed with an amine, isolated, and then brought together in a suitable solvent of low dielectric constant and low-solvating power, interconversion of A and C via a pathway involving bridges species

$$R\text{-}Mg\text{-}X \rightleftarrows R\text{-}Mg^{+} + X^{-} \qquad (2)$$

$$X^{-} + R\text{-}Mg\text{-}X \rightleftarrows R\text{-}\overset{X}{\underset{|}{Mg}}\text{-}X^{-}$$

$$R\text{-}Mg^{+} + R\text{-}\overset{X}{\underset{|}{Mg}}\text{-}X^{-} \rightleftarrows R\text{-}\underset{R}{\underset{|}{Mg}} + MgX_2$$

(Eq. 1) and via an ionic mechanism (Eq. 2) might be prevented. To test this possibility dimethylmagnesium TMED was prepared and dissolved in benzene. Since this complex is monomeric in benzene (23), the concentration of bridged species is small. When mixed with magnesium bromide TMED, which has a low solubility in benzene, redistribution was observed (Table 4). Whichever mechanism is operative for the redistribution-disproportionation, the process is too facile to be stopped by any of the methods studied.

Attempted Use of Triethylenediamine As a Complexing Agent

As previously outlined, the value of a complexing agent lies not only with its ability to prevent redistribution in the Grignard system but also with the complex it forms having different solubilities in some solvent so that fractional crystallization can be used to separate the various components. Thus, the attempted use of triethylenediamine proved unsuccessful when it was found that the dimethylmagnesium complex is insoluble in diethyl ether, n-hexane and benzene. Diethylmagnesium and magnesium bromide also form insoluble complexes with triethylenediamine.

CHAPTER IV

CONCLUSIONS

The composition of Grignard compounds in tertiary amine solvent was established by fractional crystallization and redistribution studies. The composition was shown to be best represented by the equilibrium $R_2Mg + MgX_2 \rightleftarrows 2RMgX$. This equilibrium was found to lie almost completely to the right when X = Br and, based on the generally similar results obtained when the chloride and bromide systems were fractionally crystallized, the equilibrium is also thought to lie far to the right when X = Cl. The equilibrium is not nearly so much to the right when X = I. The triethylamine complexes of R_2Mg and MgX_2 that were studied, redistribute in triethylamine and the tetramethylethylenediamine complexes that were studied, redistribute in both diethyl ether and benzene. The triethylenediamine complexes that were examined are insoluble in diethyl ether, benzene and n-hexane. For these reasons, none of these amines are suitable complexing agents for establishing the equilibrium composition of Grignard compounds.

APPENDIX

Table 1. Redistribution of Dialkylmagnesium Compounds and Magnesium Halides in Triethylamine.

Reactants	Sample	mmol Mg/g soln	mmol halogen/g soln	Mg:X*	Time (hr.)
$(C_2H_5)_2Mg + MgBr_2$	initial**	0.177	0.053	1.00:0.30	0
"	1	0.252	0.236	1.00:0.94	18.0
"	2	0.255	0.240	1.00:0.94	66.0
Calcd for 100% redistribution****		0.279	0.269	1.00:0.96	
$(C_2H_5)_2Mg + MgI_2$	initial**	0.130	0.024	1.00:0.18	0
"	1	0.186	0.159	1.00:0.86	18.0
"	2	0.168	0.138	1.00:0.82	66.0
"	3	0.164	0.128	1.00:0.78	108.0
Found for EtMgI***				1.00:0.92	
Calcd for 100% redistribution****		0.223	0.221	1.00:0.99	

Table 1. Redistribution of Dialkylmagnesium Compounds and Magnesium Halides in Triethylamine (Continued)

Reactants	Sample	mmol Mg/g soln	mmol halogen/g soln	Mg:X*	Time (hr.)
$(CH_3)_2Mg + MgBr_2$	initial**	0.180	0.045	1.00:0.25	0
"	1	0.130	0.017	1.00:0.13	0.5
"	2	0.094	0.016	1.00:0.17	4.3
"	3	0.066	0.032	1.00:0.48	21.0
"	4	0.069	0.029	1.00:0.42	46.0
Found for MeMgBr***				1.00:0.31	
Calcd for 100% redistribution****		0.299	0.299	1.00:1.00	

*X = halide ion (Br or I).

**Values for halogen content are those measured for dissolved magnesium halide prior to addition of magnesium alkyl. Magnesium concentration is the sum of that measured for the magnesium halide and that calculated for the added magnesium alkyl.

***Authentic Grignard prepared from the alkyl halide and magnesium in triethylamine. This value, when available, was inserted in the cases where the redistribution results in the precipitation of material and therefore makes difficult a meaningful comparison of the results with those calculated for 100% reaction.

****These are the values expected if all of the material goes into solution.

Table 2. Fractional Crystallization of Grignard Compounds Prepared in Triethylamine.*

Ethylmagnesium Chloride**	
Fraction	Mg:Cl:N
1	1.00:1.01:0.90
2	1.00:0.95 -
3	1.00:0.94 -
4	1.00:1.01:1.06
5	1.00:0.96 -
6	1.00:0.98 -

Ethylmagnesium Bromide	
Fraction	Mg:Br:N
1	1.00:0.99:1.02
2	1.00:1.04:1.01
3	1.00:0.93:1.01
4	1.00:0.94:1.00
5	1.00:1.00:0.94
6	1.00:0.99:0.98
7	1.00:0.95:0.99

Ethylmagnesium Iodide***	
Fraction	Mg:I
1	1.00:1.61
2	1.00:1.61
3	1.00:1.13
4	1.00:1.03
5	1.00:0.95
6	1.00:0.78

s-Butylmagnesium Chloride**	
Fraction	Mg:Cl:N
1	1.00:0.96:0.73
2	1.00:1.01:0.95
3	1.00:0.98 -
4	1.00:1.00 -

s-Butylmagnesium Bromide****	
Fraction	Mg:Br
1	1.00:1.88
2	1.00:1.35
3	1.00:1.05
4	1.00:1.04

s-Butylmagnesium Iodide***	
Fraction	Mg:I
1	1.00:1.11
2	1.00:1.01
3	1.00:1.15
4	1.00:0.81

Table 2. Fractional Crystallization of Grignard Compounds Prepared in Triethylamine.* (Continued)

t-Butylmagnesium Chloride****		t-Butylmagnesium Bromide		Phenylmagnesium Bromide**	
Fraction	Mg:Cl	Fraction	Mg:Br:N	Fraction	Mg:Br:N
1	1.00:2.06	1	1.00:2.81:1.02	1	1.00:1.05 -
2	1.00:1.13	2	1.00:1.48:0.60	2	1.00:1.22:1.02
3	1.00:1.17			3	1.00:1.25 -
4	1.00:1.09			4	1.00:1.05 -

*The data were gathered by several co-workers and are presented here in summary form to facilitate the discussion. A full presentation can be found in reference 14.

**The lack of values for nitrogen content of some of the fractions is due to an inability to completely dry these fractions. In these cases the value would be meaningless since it would include the triethylamine solvent along with the triethylamine complexed with the magnesium compound.

***None of the alkylmagnesium iodide data include values for nitrogen content. The reason for this omission is discussed in the Analysis Section of the Experimental.

****Nitrogen content was not determined.

Table 3. Fractional Crystallization of Grignard Compounds Prepared in Diethyl Ether and Quenched in Triethylamine.*

Ethylmagnesium Bromide

Fractions	Sample wt.(g)	Mg(%)	Br(%)	N(%)	Mg:Br:N
1	10.2	10.9	35.8	6.12	1.00:1.00:0.97
2	11.6	11.2	39.0	6.62	1.00:1.06:1.03
3	23.7	11.8	43.9	6.91	1.00:1.11:1.02
Calcd. for $C_2H_5MgBr \cdot N(C_2H_5)_3$		10.4	34.1	5.97	1.00:1.00:1.00
Recovery: 90.0%					

Phenylmagnesium Bromide

Fractions	Sample wt.(g)	Mg(%)	Br(%)	N(%)	Mg:Br:N
1	24.3	9.2	30.9	4.2	1.00:1.02:0.80
2	1.0	12.1	39.8	5.8	1.00:1.00:0.81
3	21.1	10.2	35.3	6.1	1.00:1.05:1.04
Calcd. for $C_6H_5MgBr \cdot N(C_2H_5)_3$		8.6	28.2	5.0	1.00:1.00:1.00
Recovery: 96.9%					

Table 3. Fractional Crystallization of Grignard Compounds Prepared in Diethyl Ether and Quenched in Triethylamine.* (Continued)

t-Butylmagnesium Chloride**

Fractions	Sample wt.(g)	Mg(%)	Cl(%)	N(%)	Mg:Cl:N
1	2.2	19.6	32.4	3.1	1.00:1.13:0.28
2	2.0	15.2	24.1	2.4	1.00:1.09:0.27
3	10.8	13.6	22.5	5.8	1.00:1.13:0.74
Calcd. for $\underline{t}$-$C_4H_9MgCl \cdot N(C_2H_5)_3$		11.2	16.3	6.4	1.00:1.00:1.00
Recovery: 99.8%					

Isopropylmagnesium Chloride

Fractions	Sample wt.(g)	Mg(%)	Cl(%)	N(%)	Mg:Cl:N
1	2.3	13.9	20.8	5.1	1.00:1.02:0.64
2	11.6	13.4	20.3	6.0	1.00:1.04:0.78
Calcd. for i-C_3-$H_7MgCl \cdot N(C_2H_5)_3$		12.0	17.5	6.9	1.00:1.00:1.00
Recovery: 83.8%					

Table 3. Fractional Crystallization of Grignard Compounds Prepared in Diethyl Ether and Quenched in Triethylamine.* (Continued)

n-Butylmagnesium Iodide***				
Fractions	Sample wt.(g)	Mg(%)	I(%)	Mg:I
1	6.3	7.1	57.7	1.00:1.56
2	1.4	7.9	48.0	1.00:1.17
3	12.1	10.8	40.2	1.00:0.71
Calcd. for $n\text{-}C_4H_9MgI \cdot N(C_2H_5)_3$		7.9	41.0	1.00:1.00
Recovery: 91.7%				

*The variation in absolute values of the elemental analysis appears to be due to the extent of drying of each sample. The important consideration here is the Mg:N ratio.

**The reason for the low nitrogen content of the fractions is not known.

***None of the alkylmagnesium iodide data include values for nitrogen content. The reason for this omission is discussed in the Analysis Section of the Experimental.

Table 4. Redistribution of Dimethylmagnesium TMED and Magnesium Bromide TMED in Benzene and Diethyl Ether.

Solvent	Sample	mmol Mg/g soln	mmol Br/g soln	Mg:X	Time (hr)
Diethyl Ether	Initial	0.180	0.013	1.00:0.07	0
Diethyl Ether	1	0.064	0.037	1.00:0.58	18.0
Diethyl Ether	2	0.062	0.046	1.00:0.74	42.0
Diethyl Ether	3	0.060	0.049	1.00:0.82	120.0
Calcd for 100% redistribution		0.338	0.344	1.00:1.02	
Benzene	Initial	0.116	0.045	1.00:0.39	0
Benzene	1	0.182	0.171	1.00:0.94	18.0
Benzene	2	0.187	0.194	1.00:1.04	45.0
Calcd for 100% redistribution		0.183	0.187	1.00:1.02	

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PART II

NATURE OF THE ASSOCIATION IN TETRAHYDROFURAN AND DIETHYL ETHER

CHAPTER I

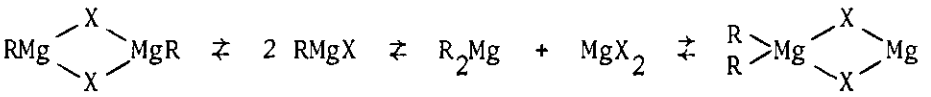
INTRODUCTION

Background

The Schlenk equilibrium (Eq. 1) is generally accepted as an

$$2\ RMgX \rightleftarrows R_2Mg + MgX_2 \qquad (1)$$

adequate description of the basic composition of Grignard compounds in polar solvents (1,2). Solutions of magnesium compounds have been found to be monomeric either in dilute diethyl ether solution (3,4) or when complexed to solvents that are stronger Lewis bases than diethyl ether such as tetrahydrofuran (5,6,7) or tertiary amines (8,9,10). However, results of recent molecular weight studies at higher concentrations in diethyl ether (3,11,12) have been interpreted as indicating association of Grignard compounds to forms higher than the monomer (Eq. 2).



(2)

Composition of the Grignard Compound in Tetrahydrofuran

Clearly, many aspects of Grignard compound composition are not as yet resolved. For example, in tetrahydrofuran the number of compounds studied is quite small and therefore the general applicability of Eq. 1 for describing the degree of aggregation in tetrahydrofuran solutions as monomeric has not been clearly established. Even for the more commonly

studied compounds (e.g. ethylmagnesium bromide), there are conflicting reports on the degree of solute association in tetrahydrofuran (5,6,7, 13).

Composition of the Grignard Compound in Diethyl Ether

Diethyl ether solutions have been examined in a little more detail. In diethyl ether, alkylmagnesium chlorides have been described as dimeric even at low concentrations (3,14) while the alkyl- and arylmagnesium bromides and iodides are monomeric at low concentration (< 0.1m) (3,4) and exhibit increased association with concentration (3,11,12). However it is not known if the bromides and iodides associate in the same manner to some stable form (dimer, trimer, tetramer, polymer etc.) or if the nature of the hydrocarbon portion of the Grignard compounds plays a major role in determining either the degree of association or the form the molecular aggregates assume in solution. Furthermore, it is not clear how the association occurs, whether by alkyl (aryl) bridges, halogen bridges, or a combination of the two.

Finally, deviations from ideal behavior (aside from that due to association of the solute) encountered in the solutions must be considered and properly interpreted. Although the danger in attributing all of the increase in molecular weight to association without due regard for these deviations is well known (15), this matter has received little attention in the past (16).

Purpose

In an attempt to clarify these issues, a comprehensive ebullioscopic study of a series of Grignard and related compounds over a wide concentration range in tetrahydrofuran and diethyl ether has been made.

CHAPTER II

EXPERIMENTAL

Instrumentation and Apparatus

Analysis of the hydrocarbons released by hydrolysis of the Grignard solutions was accomplished on a gas chromatograph (F&M Scientific Model 750) using matched columns packed with Polypak 2 (F&M Scientific).

The inert atmosphere box was manufactured by Kewaunee (Model 2C1020) and was equipped with a recirculating system to continually remove water and oxygen (17) contaminants from the nitrogen atmosphere.

The syringes which were used for making additions to the boiling point apparatus were standard glass syringes equipped with stainless steel needles.

The boiling point apparatus and nitrogen system (Figure 1) are sufficiently unique to demand detailed comments. Although the boiling point apparatus shown in Figure 1 has the same basic design as that of an ordinary Cottrell boiling point apparatus, there are some significant differences. One point worthy of note is that the apparatus is of one piece construction such that there are only three places in the apparatus where outside connections must be made. These include two ground glass joints, one for a Beckman thermometer, one for connection to a nitrogen system, and an opening for a septum cap. The septum cap allows the periodic addition of samples (in solution via syringe) to the apparatus without exposing the sensitive material to the atmosphere. Note

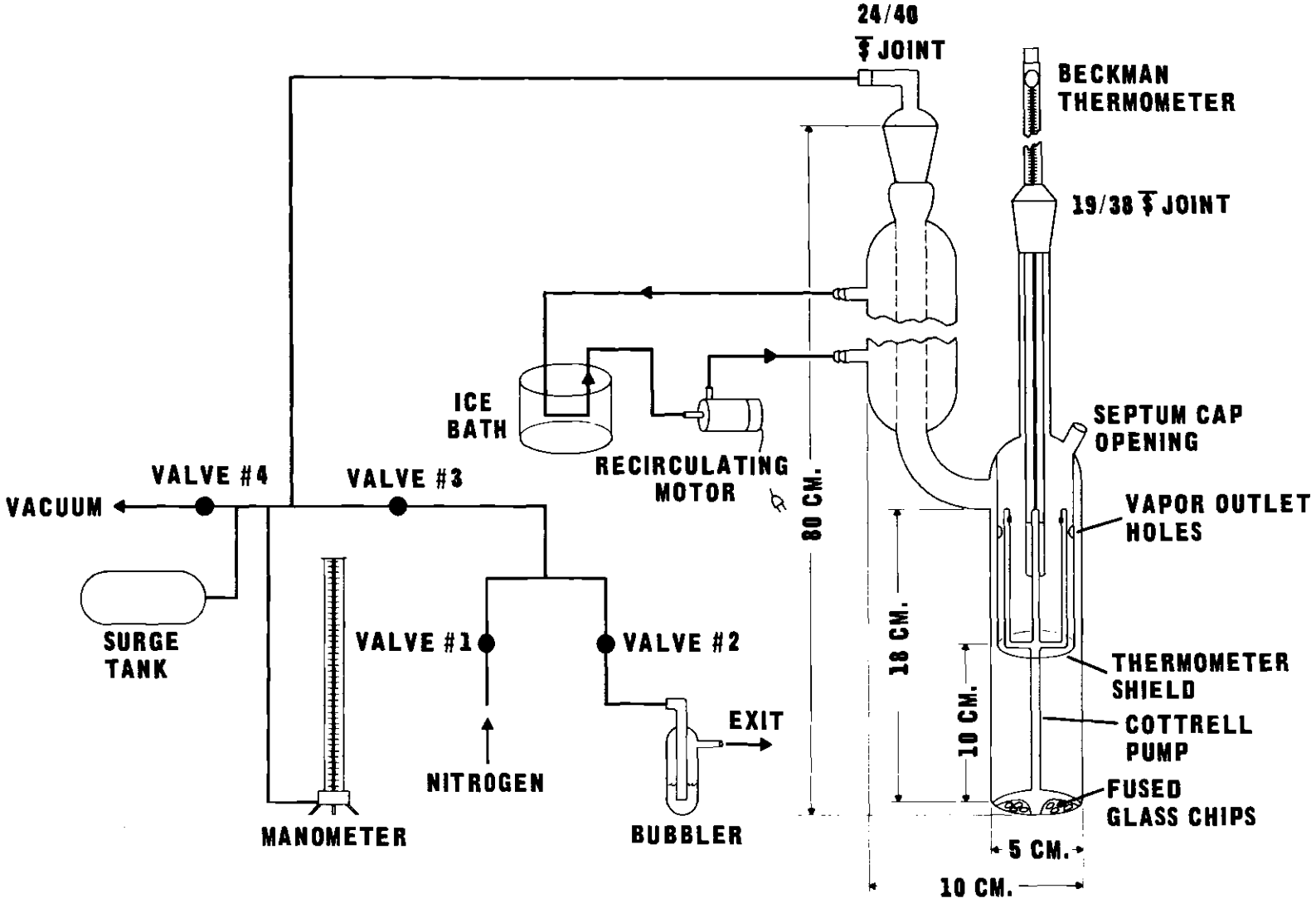


Figure 1. Ebullioscopic Apparatus

that the septum cap opening is positioned between the condensate shield and the thermometer; this arrangement allows thorough mixing of the samples with the boiling solution. The condensate shield extends to just below the bottom of the mercury bulb of the thermometer where it protects the bulb from contact with cold condensate. When the study is conducted with a low boiling solvent such as diethyl ether, the condenser is connected to a recirculating motor and cooled with ice water to eliminate solvent loss and excessive solvent holdup in the condenser. The bulb of the thermometer is continually bathed with boiling solvent by the pump, and superheating of the solution is minimized by the glass chips fused to the bottom of the solvent chamber.

The remainder of the equipment in Figure 1 comprises the nitrogen system which is designed to allow operation of the apparatus at any pressure that is desired. This sytem is constructed with copper tubing with all connections being made with brass compression fittings. Where a connection must be made between the copper line and either hose fittings or glass tubing, a short piece of securely clamped pressure tubing is used. The surge tank has a capacity of about 20 liters and can withstand a vacuum of at least one millimeter. An oxygen storage tank of the type used by the United States Air Force meets these requirements. The surge tank acts as a damper for small pressure changes in the system and therefore aids in maintaining a constant pressure. The manometer is a precision Wallace and Tiernan Gauge that can be read with high accuracy; it has an adjustment that compensates the pressure scale for temperature changes in the laboratory. The valves are brass-seated and must be of high quality in order for a constant pressure, either higher

or lower than atmospheric pressure, to be maintained in the system. The oil bubbler acts as a terminal gas gauge in that it monitors the rate of nitrogen flow past the system.

Chemicals

Bromine (Matheson Reagent), iodine (Baker Analyzed) and organomercury compounds (Metallomer) were used without further purification.

The alkyl and aryl halides (Eastman Reagent and p-Bromobenzotrifluoride from Pierce) were dried over Na_2CO_3 prior to distillation through an 18-inch packed column under nitrogen.

Ether-washed triply sublimed magnesium (Dow) was employed in all of the preparations.

Diethyl ether (Fisher Anhydrous) was distilled from lithium aluminum hydride and tetrahydrofuran (Fisher Certified) from sodium aluminum hydride through a two-foot packed column under dry oxygen-free nitrogen.

Analyses

All of the solutions were analyzed for magnesium by titration with EDTA; solutions of the Grignard compounds and magnesium halides were analyzed for halogen by the Volhard method. Samples of the Grignard solutions were hydrolyzed in ampoules containing either benzene or diethyl ether to trap released hydrocarbons. The organic layer was analyzed to glpc to determine the amount of coupling product and unreacted starting material; the yield of Grignard was consistently greater than 96%.

Preparations and Procedures

General Procedures

All manipulations of the chemicals and reaction solutions were carried out either in a glove box (dry nitrogen atmosphere) or on the bench top in sealed systems under nitrogen. All equipment that came in contact with the chemicals and reaction solutions was dried by flash flaming under vacuum or under a flow of nitrogen; all reactions were then carried out under a nitrogen blanket.

Preparation of the Grignard Compounds

The Grignard compounds were prepared in 500 ml round-bottom one-neck flasks containing a 10 to 100 per cent excess of magnesium and a magnetic stirring bar. Gaseous halides were first passed through a tube of NaOH and drying agent (molecular seive 4 A) and then introduced into the reaction vessel through a side arm at the bottom of a Dry Ice condenser. The condenser was connected to the reaction vessel via a Claissen adapter with a parallel side arm which held an addition funnel containing 400 ml ether. Liquid halides were added via an addition funnel which was connected to the reaction vessel by two Claissen adapters with parallel side arms. The other two arms held an addition funnel with 400 ml ether and a water-cooled condenser.

The reactions were initiated by adding 50 ml ether and a small portion of the halide. In each case the reaction started either spontaneously or after gentle warming; in no case was it necessary to add any kind of initiator. Enough halide was added in each case to prepare a one molar solution. The products were concentrated by vacuum distilling the solvent at room temperature using a simple distillation

apparatus with a Dry Ice-acetone cooled receiver. The final solutions, which were clear and colorless (except for the arylmagnesium halides which were slightly colored), were not separated from the unreacted magnesium but were sampled directly from the reaction vessel.

Preparation of the Dialkyl- and Diarylmagnesium Compounds

Diphenylmagnesium was prepared in the same manner as dimethyl- and diethylmagnesium (18,19) as described in Part I of this thesis except that the reaction was conducted at 160°C by heating with an oil-bath. The solutions were concentrated and sampled in the same manner as the Grignard compounds.

Preparation of the Magnesium Halides

The preparation of the magnesium halides (18,19) has already been described in Part I of this thesis; the procedure used for magnesium bromide in THF was identical to that used in diethyl ether. Studies with magnesium bromide prepared either by bromine addition to magnesium (18,19) or by exchange between mercuric bromide and magnesium (19) produced identical molecular weight data.

Operation of the Boiling Point Apparatus

Due to the unique character of the apparatus and the experiments conducted with it, a complete account of all of the steps necessary to assemble the apparatus and duplicate the measurements will be given.

After placing the apparatus in the nitrogen system as shown in Figure 1, the properly adjusted Beckman thermometer was seated with a minimum of high vacuum stopcock grease and the septum cap was inserted and secured with a small piece of wire. On the initial run all connections were checked for leaks by closing valves 2 and 4 and opening

valve 3. Valve 1 was opened slowly until the manometer read a pressure somewhat higher than atmospheric; then valve 1 was closed. The manometer was read and then rechecked in a few minutes to see if there was a pressure change. If some leakage was indicated the location was determined with a soap solution. When the pressure remained constant for five minutes, the system was considered ready for operation.

After determining that the system was tight, the next step was to dry the system and fill it with nitrogen; this was accomplished by closing valve 3, starting the vacuum pump, and slowly opening valve 4. After evacuating the system the glass portion of the apparatus was dried by carefully sweeping with a bunsen burner flame. Extreme caution was exercised here since prolonged heating at one point on the surface of the glass could crack the apparatus. The vacuum was maintained until the glass had cooled; then the system was filled with nitrogen by closing valve 4, opening valves 1 and 2 (a fast flow of gas through the bubbler was maintained) and then opening valve 3 at a rate that did not allow the oil in the bubbler to enter the line. This procedure was repeated at least two more times.

Since the next step involved the use of syringes, a brief description of this operation will be given. The syringes were dried placing the hot syringes in a dry box entry port which was then evacuated. The syringe needle was capped after the sample was withdrawn into the syringe by inserting the needle into a small section cut from a septum cap. When the sample was injected into the apparatus, the needle was pushed through the rubber section, through the septum cap on the ebulliscopic apparatus and on into the system for injection. This method elimi-

nated loss of sample during the transfer.

The final purging step was inititated by adding twenty to twenty-five milliliters of the solvent to the apparatus. When making additions to the apparatus, valves 3 and 2 were opened with a small nitrogen flow through valve 1. After adding the solvent the evacuation procedure was repeated, followed by flaming and refilling with nitrogen. This final purging step swept the moisture out of the condenser and internal parts that were not efficiently heated from the outside.

The first material introduced was the solvent (diethyl ether or THF). The quantity of solvent used depended on the efficiency of the solvent pump because it was absolutely necessary that the bulb of the thermometer be continually bathed with boiling solvent. The system was heated with a heating mantle and the powerstat setting was as low as possible to avoid superheating. Precautions against drafts on the apparatus were taken by wrapping the solvent chamber up to the thermometer with insulating material.

The initial reading made was the boiling point of the pure solvent at the desired pressure. Thus, valves 1 and 4 were closed and valves 2 and 3 were opened. After the pressure had dropped below the desired pressure, valve 2 was closed and valve 1 opened slowly until the correct pressure was reached. At this point valve 1 was closed and the system brought to thermal equilibrium. This required five minutes of boiling at the desired pressure. The pressure was rechecked before reading the thermometer; the manometer and thermometer were gently tapped before making the reading. The observed boiling point was considered final only when it could be reproduced at least twice by dropping the

pressure and then readjusting it to the desired level. After establishing the boiling point of the solvent, a weighed portion of the solution to be studied was added by following the same sequence of steps used with the solvent addition. Several additions of the sample were needed to obtain a value for the molecular weight at several concentrations, but the amount of material added was limited in order to avoid contact of the solution with the thermometer bulb. If contact had occurred, the temperature registered would not be the desired liquid-vapor equilibrium temperature but would be that of the solution which could have been slightly superheated.

Calculations

By making the assumption of an ideal but not necessarily a dilute solution, one can derive from the Clapeyron-Clausius relationship an equation relating the observed boiling point elevation, ΔT_B, to the mol fraction, X_E, of solute(s) in solution (Equation 3).

$$X_E = 1 - e^{-\frac{\Delta T_B M_1}{1000\ K_B}} \tag{3}$$

The other terms in the equation are: M_1, the mol wt of solvent; and K_B, the molal boiling point elevation constant (2.01 for diethyl ether at 740.0 mm Hg; 2.20 for tetrahydrofuran at 740.0 mm Hg). The use of this extended equation for the calculations was necessitated by the high solute concentrations which invalidate a number of dilute solution approximations employed in the derivation of simpler relationships. This matter has been examined in detail recently (20).

The results are expressed in terms of solute association indicated as an i-value. If there is a single solute species in the solution, the i-value is the ratio of the mol wt of this species to the formula wt of the solute. If there is more than one solute species in solution, the i-value is the ratio of the number-average molecular weight of the solutes to the formula wt of the solute. It should be noted that the number-average mol wt is numerically equal to the mol wt of a single species which would give a boiling point equivalent to that observed experimentally. Equation 4 was used for the computation of the i-values. The

$$i = \frac{W_2 M_1}{W_1 M_2} \left(\frac{1}{e^{\frac{\Delta T_B M_1}{1000\ K_B}} - 1} \right) \qquad (4)$$

additional terms are: W_2, grams of solute; W_1, grams of solvent; and M_2, formula wt of solute.

Certain features of the calculation of i-values by Equation 4 deserve further comment since there is the complicating feature of complexation between solute and solvent. This complexation in solution has been demonstrated in a number of ways including the use of spectral techniques (21,22,23) and the use of optically active ethers (24). While it is clear in principle (2) that complexed solvent molecules should be included as an integral part of the solute species, the actual number of solvent molecules in any given case is generally not known. The degree of solvation assumed has a direct effect on the i-values calculated from

Equation 4. The assumption does not affect the ratio W_2/M_2 in the equation, although it affects the individual values of W_2 and M_2; but rather affects the value of W_1, the amount of free solvent. If too little solis ascribed to the solute, the amount of free solvent is too high and the resulting i-values will be lower than the correct values. Conversely, if too much solvent is included with the solute in computing the formula wt, the calculated value of i is higher than the correct value.

There is ample information available on the degree of complexation of solvent with solute in the solid state. The complexes with tetrahydrofuran, diethyl ether and tertiary amines have been characterized (8,9, 10,25,26,27,28) as monosolvates through hexasolvates; the degree of complexation apparently varies with the solvent and the identity of the magnesium compound. However, it is not clear that the degree of solvation in solution can be deduced from the extent of complexation in the solid state.

In the few instances where solvation data are available for solutions there is no agreement on the degree of solvation since similar magnesium compounds complexed with tetrahydrofuran have been characterized as both monoetherates (29,30) and dietherates (31). Logically, one might suggest that the monomers are dietherates (tetracoordinate magnesium) and that association occurs with concurrent displacement of a solvent molecule by the bridging group to form monosolvated multimers (tetracoordinate magnesium). However, it is possible that dissolvated monomers (tetracoordinate magnesium) associate to dissolvated multimers if the magnesium atoms were pentacoordinate as recently suggested (32) for dimethylmagnesium in its reaction with benzophenone.

Since the choice of the degree of solvation is somewhat arbitrary at this point, it is important to compare the results obtained when different extents of solvation are assumed. Figure 2 and Table 1 show that the calculated i-values in dilute solution are not very sensitive to the assumed degree of solvation. Although the differences in the i-value curves for the mono- and dietherates are magnified somewhat at higher concentrations, the relative positions of the i-value curves for the various compounds are unchanged by the choice. This observation, coupled with the insensitivity of the i-value curves to the formula assumed in dilute solution, means that the arguments, which are based on a comparison of the i-value curves for the various compounds, are valid regardless of the degree of solvation. Therefore, the formulation of the solute as a monoetherate has been chosen for the computation of the i-values. It is felt that this is the best compromise since a monoetherate represents the minimum degree of solvation; and therefore all of the compounds will be solvated at least to this extent. The experimental data and the results of these calculations are presented in Tables 5 (tetrahydrofuran solutions) and 6 (diethyl ether solutions).

Equilibrium constants were calculated from the association data by using equations derived for model association systems. The derivation of these relationships for use with vapor phase osmometry data has been presented in detail (33); similar models have been used before for studies with other systems (34,35). The basic assumption made in deriving these equations is that the apparent molecular weight is solely a function of association of the solute without any contribution by deviations from ideality. Model I assumes a polymeric association with the

same equilibrium constant for each step. Model II is based on the assumption of monomer in equilibrium with a single associated form; the data were analyzed for systems ranging from monomer:dimer (n = 2) through monomer:hexamer (n = 6).

Model I	Model II
$A_n + A_1 \rightleftarrows A_{n+1}$	$nA \rightleftarrows A_n$
$K_1 = \frac{X_S - X_E}{X_E^2}$	$K_n = \frac{(X_S - X_E)(n-1)^{n-1}}{(nX_E - X_S)^n}$

The term X_S is the stoichiometric mole fraction of solute (based on the formula weight of the solute and the actual concentration in solution) and X_E, the experimental mole fraction, is given by Equation 3. Separate calculations were made both for the monoetherate and the dietherate forms as solute, and were computed for the entire concentration range.

The assumption of ideal behavior inherent in the derivations means that the equilibrium constants calculated from the data in dilute solution will have greater validity than those calculated for the more concentrated solutions. Therefore, in addition to examining the consistency of the equilibrium constants calculated for all concentrations, particular attention was paid to the constancy of the values in the more dilute range. Generally it was found that if the equilibrium constants for a particular model were consistent in dilute solution, then they were reasonably consistent overall and that model was chosen as the best description of the system.

CHAPTER III

RESULTS AND DISCUSSION

Composition of Grignard Compounds in Tetrahydrofuran

Figure 3 shows the association expressed as an i-value (apparent molecular weight divided by the monoetherate formula weight) for selected Grignard and related compounds in tetrahydrofuran. The i-values are clustered around the monomer value (i=1.0) and display a small concentration-dependent line curvature. The lack of significant curvature argues against an equilibrium-type association since the i-values would be expected to increase with concentration. Further, the i-values for an equilibrium-type association would be expected to show a noticeable temperature effect. However, the i-values reported here agree well with those reported at lower temperatures (5) and a study of the same solution at two different temperatures (6,7) failed to reveal a temperature effect. Although there appears to be no evidence for an equilibrium system of association, the solute could possibly form a stable multimer e.g. dimers, with the observed i-values reflecting large negative deviations of the solution from ideality; such behavior is not unreasonable for systems of this type (36). However, dimer formation is not compatible with the fact that the i-value curves all extrapolate with reasonable accuracy to an i-value of one. Since deviation from ideal behavior would be at a minimum at high dilution, an extrapolated i-value of two would be expected for a solution of stable dimers. Finally, spectroscopic studies (26)

have been unable to find any evidence that magnesium compounds associate to any form in tetrahydrofuran solution. Therefore all the evidence clearly favors the interpretation that Grignard and related magnesium compounds are monomeric in tetrahydrofuran and that the observed slight departure of the i-value curves from the ideal monomer value is due to deviations from ideal behavior.

Composition of Grignard Compounds in Diethyl Ether

Alkylmagnesium Chlorides

In agreement with studies at much lower concentrations (3,14), the i-value curves for the alkylmagnesium chlorides in diethyl ether (Figure 4) extrapolate to an i-value much greater than one at high dilution, a result unlike that observed in tetrahydrofuran. The fact that the i-values do not extrapolate to a value near one is not compatible with an equilibrium-type association. Further, the extrapolated i-value argues against solutions of monomers or stable trimers displaying deviations from ideality. Therefore, the best conclusion is that the alkylmagnesium chlorides in diethyl ether are essentially completely dimerized over the entire concentration range.

These conclusions are in harmony with the results obtained by calculating equilibrium constants with equations derived for model association systems. The data for all of the alkylmagnesium chlorides were tested and were found to fit neither a polymeric association model (Model I) nor a monomer:dimer through a monomer:hexamer model (Model II with n=2 through n=6) as indicated by a wide variation in the equilibrium constants for each compound. The results of these calculations are

shown for t-BuMgCl (Table 2).

Finally, it should be noted that the differences observed in the association curves at higher concentrations are probably a reflection of varying degrees of deviation from ideal behavior rather than a real difference in the association phenomena. It is interesting to note that the t-butylmagnesium chloride solution appears to behave in a near ideal manner since the i-values lie nearest the dimer value of two. Although an argument might be made that the bulk of the t-butyl group is inhibiting the interactions responsible for deviation from Raoult's law, it seems more likely that the apparent ideal behavior of the t-butylmagnesium chloride solution results from a fortuitous balancing of the various factors that influence deviation from ideal behavior.

Alkyl- and Arylmagnesium Bromides and Iodides

Unlike the association curves for the alkylmagnesium chlorides in diethyl ether, the curves for several alkyl- and arylmagnesium bromides and iodides in diethyl ether (Figure 5) extrapolate to an i-value of one at high dilution. Although this is reminiscent of the behavior of the tetrahydrofuran solutions (Figure 3), the i-values for the diethyl ether solutions (Figure 5) are noticeably larger even in dilute solution and continue to increase rapidly with concentration. This same type of behavior is observed for other magnesium compounds in diethyl ether, especially dimethylmagnesium and the magnesium halides (Figure 6).

As noted earlier this is the type of behavior expected if the solute were either associated in a concentration-dependent equilibrium system or monomeric and displaying large deviations from ideal behavior. Although a decision on the importance of either factor would be very

difficult based solely on the molecular weight data, a consideration of other data indicates that this type of i-value curve is representative of a high degree of solute association.

For example, it has been observed that the τ-values for dimethylmagnesium in diethyl ether are concentration dependent (16,37) and this has been attributed to dissociation of polymeric dimethylmagnesium with dilution. A similar but less pronounced shift has been observed (37) on dilution of methylmagnesium iodide in diethyl ether. Perhaps the best spectroscopic evidence for association in diethyl ether is the presence of a concentration dependent band in the infrared spectrum (26) of a diethyl ether solution of dimethylmagnesium. The intensity of the band increases with concentration and has been ascribed to associated forms of dimethylmagnesium. This band is not present in tetrahydrofuran solutions. Some indirect evidence for association is found in heat of mixing data (5,11) which have been interpreted in terms of Grignard compound association in diethyl ether.

Exmaination of the data in Figure 5 reveals that the i-value curves are similar at low concentrations but, as the concentration is increased, a change from a positive to a negative slope is observed. This change in slope is not good evidence for the formation of a stable associated form in a monomer:dimer or monomer:trimer equilibrium since this would be indicated by flattening of the i-value curves rather than by passage of the curves through a maximum. Instead, this curvature is best understood in terms of a high degree of solute-solvent interaction leading to negative deviation from Raoult's law. The decreasing i-values at higher concentrations are expected if the solute and solvent molecules

are interacting so as to reduce the amount of free solvent in solution. When it is realized that there are approximately seven molecules of solvent for every molecule of anhydrous solute in a 2.0 m etheral solution, it is obvious that even a small interaction will cause a relatively large reduction in the percentage of free solvent.

A comparison of the i-values for a diethyl ether solution of n-decylmagnesium bromide (Figure 7) with those for ethylmagnesium bromide supports this conclusion. Although n-decylmagnesium bromide sould exhibit approximately the same degree of association as ethylmagnesium bromide, the i-values for the former are much smaller and the slope of the curve changes from positive to negative at a much lower concentration. This is in agreement with the trend observed in Figure 5 i.e., the i-values start decreasing at a lower concentration as the hydrocarbon chain is lengthened. From the data presented in Figure 2, it is clear that no reasonable increase in the amount of solvent ascribed to formal complexation with n-decylmagnesium bromide will cause a significant increase in the i-values. Apparently, then, the negative deviations observed in Figures 5 and 7 are best viewed as arising from some non-specific interaction, such as that due to van der Waal's forces, between the solute and solvent molecules.

Further evidence against the presence of a stable associated form in equilibrium with monomer in the diethyl ether solutions of alkyl- and arylmagnesium bromides and iodides is provided by the equilibrium constants calculated for model systems. Reasonably good agreement is obtained at all concentrations (Table 3) for the polymeric association model (Model I) which is based on the formation of multimers in solution.

Table 4 shows in further detail the equilibrium constant calculations for a typical Grignard compound (methylmagnesium bromide) which demonstrates that the interpretation of the data as representing a polymeric association is superior to any other possibility. It should be noted that the data do not distinguish the formation of linear polymers from the formation of transient cyclic dimers, trimers, etc. or a combination of linear and cyclic polymerization.

Success in identifying the bridging group depends on the validity of comparing the i-values for diethyl ether solutions of dissimilar compounds. Specifically, the magnesium halides, the magnesium alkyls (aryls) and the alkyl (aryl) Grignard compounds should differ considerably in polarity and the degree to which the i-values reflect this difference must be considered. Information on polarity effects can be found in Figure 8 where it is seen that the i-values for phenylmagnesium bromide and p-trifluoromethylphenylmagnesium bromide in diethyl ether are little changed although there is certain to be a large difference between the two compounds with respect to polarity. The difference between the i-value curves is about the same as that observed with the other Grignard compounds (Figure 5). The small depression of the i-values at high concentrations for p-trifluoromethylphenylmagnesium bromide is probably similar to, but much smaller than, the effect observed with n-decylmagnesium bromide (Figure 7); that solute-solvent interactions can be increased by increasing the polarity of the solute is not surprising in a polar solvent such as diethyl ether.

Although the polarity differences apparently have little influence on the i-values, it is evident from the data presented in Figure 7

that the i-values are influenced by a change in the identify of the hydrocarbon portion of the solute molecule. Thus, while comparison of the i-values for dimethyl- and diethylmagnesium (Figure 6) seems appropriate, a similar comparison with the data for diphenylmagnesium is difficult.

A better understanding of the bridging abilities of the various groups is achieved by comparing the i-values for a homologous series of magnesium compounds. Thus, the data at low concentration in Figure 9 clearly demonstrate that the methylmagnesium halides associate by both methyl and halogen bridges. The bridging efficiency of the methyl group in organomagnesium compounds has been indicated by other evidence (38) and is well established in organoaluminum chemistry. The association of the phenylmagnesium halides (Figure 10) and the ethylmagnesium halides (Figure 11) is mainly through the halogen atom; the weakness of ethyl and phenyl bridges in diethyl ether becomes even more apparent when Figures 10 and 11 are compared with Figure 9 for the methyl compounds.

The association curve for mesitylmagnesium bromide* is shown in Figure 12. The very small i-values, particularly in dilute solution, are clearly due to the bulk of the mesityl group effectively destroying the type of association observed for the unhindered phenylmagnesium bromide. Precisely what steric requirements are to be met before this occurs is not clear since the i-values for t-butylmagnesium bromide (Figure 13) are a little larger than those for ethylmagnesium bromide. The differ-

*Previously it was reported (3) that mesitylmagnesium bromide associates in diethyl ether solution to a higher degree than ethylmagnesium bromide. Although the reasons for this discrepancy are not known, high values are always suspect due to the well-documented effect of oxygen (12,39) which causes the apparent molecular weight of these solutes to increase by forming highly associated alkoxide derivatives.

ences between the i-values for t-butylmagnesium bromide and t-butylmagnesium chloride indicate that the steric requirements play a small role in determining the form of the association since the t-butylmagnesium bromide curve shows all the characteristics found for the other bromides and iodides in diethyl ether rather than those of the dimeric chlorides.

CHAPTER IV

CONCLUSIONS

Ebullioscopic data are presented for tetrahydrofuran and diethyl ether solutions of several Grignard and related magnesium compounds over a wide concentration range. Analysis of the data is accomplished by observing the change in association (i) with concentration and by consideration of the constancy of the equilibrium constants calculated for several possible descriptions of the associated system. The expected non-ideality of the solutions studied was considered in the interpretation of the data. While all of the compounds studied were found to be monomeric in tetrahydrofuran, the alkyl- and arylmagnesium bromide and iodides were found to be monomeric in diethyl ether only at low concentration, (< 0.1 m) exhibiting in general an increase in association with concentration. Interpretation of the data indicates that these compounds are associated in a polymeric fashion. In contrast the alkylmagnesium chlorides in diethyl ether associate to form stable dimers with the association insensitive to concentration changes. Comparison of the data for magnesium halides and dialkylmagnesium compounds in diethyl ether indicates that, except for the methyl compound, association is considerably stronger for the magnesium halides than for the dialkylmagnesium compounds. Thus, except for methylmagnesium halides, Grignard compounds associate with bridging mainly through the halogen atom. The methylmagnesium halides are exceptional since methyl bridging is strong enough

in diethyl ether to permit association by bridging through either the methyl group or the halogen atom. Although the steric requirements of the alkyl group has some effect on the association of Grignard compounds, the effect is generally small compared to the effect of halogen or solvent.

APPENDIX

Table 1. Variation of i-Values with Formula Weight for Ethylmagnesium Chloride in Tetrahydrofuran and Diethyl Ether.

Monoetherate (THF)		Dietherate (THF)	
Association, i	Concn., m	Association, i	Concn., m
1.18	0.357	1.19	0.367
1.22	1.152	1.33	1.257
1.15	1.930	1.34	2.243
1.11	2.415	1.34	2.924
Monoetherate (Et_2O)		**Dietherate (Et_2O)**	
Association, i	Concn., m	Association, i	Conc., m
1.77	0.127	1.78	0.128
1.96	0.341	2.02	0.350
2.14	0.615	2.25	0.644
2.35	1.019	2.55	1.103
2.54	1.431	2.84	1.602
2.68	1.914	3.12	2.231
2.75	2.284	3.31	2.751
2.81	2.672	3.51	3.334

Table 2. Equilibrium Constants Calculated for t-Butylmagnesium Chloride in Diethyl Ether

X_S	X_E	K_1	K_2	K_3
0.00725	0.00390	220.	1.10×10^4	152.
0.0205	0.0104	93.2	9.57×10^4	32.7×10^3
0.0372	0.0184	55.4	13.6×10^4	12.8×10^3
0.0575	0.0283	36.5	3.55×10^4	5.68×10^3
0.0750	0.0367	28.5	1.42×10^4	3.56×10^3
0.0819	0.0398	26.6	0.794×10^4	3.19×10^3
0.0963	0.0469	22.4	0.798×10^4	2.26×10^3
0.1113	0.0545	19.1	1.06×10^4	1.60×10^3
0.1238	0.0610	16.9	1.99×10^4	1.21×10^3

K_4	K_5	K_6
$615. \times 10^4$	2.25×10^{-8}	4.38
45.5×10^4	$518. \times 10^4$	13.2×10^6
9.59×10^4	60.6×10^4	5.87×10^{-2}
2.73×10^4	11.2×10^4	28.9×10^6
1.30×10^4	4.09×10^4	4.86×10^6
1.06×10^4	3.06×10^4	2.87×10^6
0.639×10^4	1.57×10^4	0.896×10^6
0.395×10^4	0.835×10^4	0.303×10^6
0.270×10^4	0.514×10^4	0.132×10^6

Table 3. Equilibrium Constants Calculated for Polymeric Association (Model I).

Compound*	K_1**	
CH_3MgBr	43.2 ± 6.7	15.6%
CH_3MgI	41.0 ± 6.1	14.9%
C_2H_5MgBr	23.6 ± 8.3	35.2%
C_2H_5MgI	24.7 ± 6.4	25.9%
C_6H_5MgBr	64.8 ±15.8	24.4%
C_6H_5MgI	63.7 ±13.5	21.2%

*Formula weight based on monoetherate. Values for dietherate show similar deviations.

**Mole fraction scale. Uncertainties are standard deviation of the mean.

Table 4. Equilibrium Constants Calculated for Methylmagnesium Bromide in Diethyl Ether

X_S	X_E	K_1	K_2	K_3
0.0108	0.00830	36.2	74.0	3.55×10^3
0.0291	0.0173	39.5	392.	3.99×10^3
0.0526	0.0240	49.7	1330.	15.8×10^3
0.0803	0.0310	51.3	147.	97.0×10^3
0.1053	0.0371	49.5	70.6	$1260. \times 10^3$
0.1254	0.0414	49.0	46.3	-1.98×10^{-2}
0.1442	0.0461	46.2	36.2	$-1880. \times 10^3$
0.1613	0.0514	41.6	32.1	$-1240. \times 10^3$
0.1766	0.0568	37.1	30.2	$-1970. \times 10^3$
0.1926	0.0632	32.4	29.6	$-19900. \times 10^3$

K_4	K_5	K_6
8.90×10^4	14.6×10^5	0.326×10^7
4.12×10^4	3.04×10^5	2.95×10^{-2}
7.29×10^4	3.30×10^5	14.6×10^7
12.2×10^4	3.40×10^5	7.96×10^7
17.8×10^4	3.29×10^5	4.75×10^7
28.9×10^4	3.71×10^5	4.01×10^7
33.9×10^4	3.29×10^5	2.60×10^7
25.6×10^4	2.19×10^5	1.25×10^7
16.5×10^4	1.34×10^5	0.568×10^7
8.84×10^4	0.722×10^5	0.220×10^7

Table 5. Association of Grignard and Related Magnesium Compounds in Tetrahydrofuran at Approximately 65°C

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
Ethylmagnesium Chloride				
0.357	39.408	2.269	0.668	1.18
1.152	47.135	8.744	2.005	1.22
1.930	58.334	18.127	3.483	1.15
2.415	68.460	26.613	4.447	1.11
t-Butylmagnesium Chloride				
0.259	41.011	2.007	0.495	1.14
0.693	48.900	6.407	1.235	1.21
1.106	59.841	12.508	1.906	1.24
1.441	73.116	19.910	2.580	1.18
1.655	85.181	26.638	3.015	1.15
1.816	97.324	33.409	3.353	1.13
1.943	109.508	40.204	3.603	1.12
Phenylmagnesium Bromide				
0.131	41.476	1.380	0.263	1.09
0.307	49.622	3.866	0.591	1.13
0.519	64.936	8.542	1.001	1.12
0.649	80.072	13.163	1.233	1.13

Table 5. Association of Grignard and Related Magnesium Compounds in Tetrahydrofuran at Approximately 65°C (Continued).

Methylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.230	42.772	1.647	0.438	1.15
0.462	50.051	3.865	0.860	1.16
0.778	65.152	8.465	1.401	1.19
0.994	82.089	13.624	1.803	1.18
1.126	97.636	18.361	2.056	1.16
1.218	112.463	22.878	2.203	1.17
1.286	126.619	27.190	2.343	1.16

Ethylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.188	41.562	1.604	0.390	1.05
0.485	51.520	5.132	0.922	1.14
0.763	66.439	10.417	1.405	1.17
0.945	81.878	15.887	1.755	1.15
1.066	96.892	21.207	2.003	1.13
1.148	110.655	26.082	2.138	1.14
1.217	125.892	31.480	2.291	1.13

Table 5. Association of Grignard and Related Magnesium Compounds in Tetrahydrofuran at Approximately 65°C (Continued).

Diethylmagnesium

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.323	39.485	1.972	0.742	0.95
0.850	44.535	5.847	1.985	0.91
1.278	49.710	9.819	3.100	0.86
1.624	54.854	13.767	4.058	0.82
1.764	57.264	15.616	4.475	0.80

Diphenylmagnesium

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.165	41.269	1.711	0.393	0.92
0.397	49.011	4.873	0.833	0.98
0.658	62.182	10.253	1.495	0.94
0.842	76.698	16.182	1.915	0.94

Magnesium Bromide*

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.060	46.631	0.716	0.135	0.98
0.119	63.889	1.948	0.233	1.12
0.166	90.469	3.844	0.311	1.17
0.191	117.032	5.740	0.418	1.00
0.207	142.163	7.533	0.441	1.02

*Data not shown graphically.

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C.

Isopropylmagnesium Chloride

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.189	58.274	1.950	0.198	1.90
0.580	60.353	6.195	0.558	2.06
1.154	63.688	13.002	1.023	2.22
1.743	67.519	20.825	1.463	2.33
2.211	70.913	27.751	1.813	2.37
2.583	73.855	33.758	2.093	2.38
2.960	77.101	40.385	2.383	2.39

t-Butylmagnesium Chloride

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.098	60.472	1.138	0.107	1.86
0.282	61.928	3.336	0.284	1.99
0.521	63.926	6.360	0.502	2.06
0.823	66.650	10.480	0.777	2.10
1.094	69.302	14.489	1.013	2.13
1.204	70.428	16.191	1.100	2.15
1.437	72.971	20.036	1.303	2.16
1.690	75.930	24.509	1.520	2.17
1.906	78.657	28.634	1.707	2.17

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

Ethylmagnesium Chloride

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.127	60.947	1.262	0.144	1.77
0.341	62.377	3.464	0.347	1.96
0.615	64.311	6.444	0.569	2.14
1.019	67.392	11.192	0.857	2.35
1.431	70.855	16.526	1.110	2.54
1.914	75.393	23.518	1.400	2.68
2.284	79.287	29.518	1.620	2.75
2.672	83.822	36.504	1.844	2.81

t-Butylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.084	57.768	1.137	0.128	1.31
0.191	59.453	2.672	0.266	1.43
0.373	62.553	5.497	0.441	1.69
0.581	66.504	9.097	0.596	1.94
0.771	70.575	12.807	0.716	2.13
0.941	74.689	16.557	0.826	2.26
1.095	78.792	20.295	0.921	2.35
1.229	82.805	23.953	1.008	2.40
1.351	86.809	27.602	1.086	2.45
1.494	92.018	32.349	1.183	2.48

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

Ethylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.050	55.979	0.581	0.098	1.03
0.260	56.913	3.066	0.390	1.33
0.588	58.441	7.132	0.662	1.77
1.021	60.583	12.830	0.925	2.18
1.428	62.743	18.578	1.138	2.47
1.789	64.799	24.047	1.345	2.61
2.123	66.818	29.419	1.555	2.67
2.438	68.849	34.821	1.785	2.66
2.765	71.084	40.766	2.056	2.60
3.074	73.340	46.767	2.356	2.51

Phenylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.071	59.468	1.081	0.120	1.19
0.207	61.176	3.230	0.280	1.47
0.227	62.100	4.393	0.340	1.62
0.516	65.471	8.635	0.490	2.10
0.738	68.939	12.999	0.580	2.53
0.938	72.405	17.360	0.643	2.90
1.121	75.869	21.719	0.697	3.19
1.288	79.350	26.100	0.750	3.40
1.436	82.717	30.337	0.790	3.60

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

p-Trifluorobenzomagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.211	59.520	4.059	0.242	1.74
0.559	61.147	11.054	0.490	2.27
1.038	63.533	21.323	0.727	2.82
1.636	66.794	35.350	1.045	3.09

n-Decylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.093	57.809	1.725	0.168	1.11
0.252	58.699	4.737	0.410	1.23
0.489	60.075	9.398	0.742	1.31
0.790	61.917	15.634	1.125	1.38
1.066	63.712	21.711	1.555	1.34
1.342	65.609	28.133	1.987	1.31
1.591	67.426	34.286	2.415	1.27
1.835	69.305	40.649	2.915	1.20
2.062	71.151	46.898	3.410	1.14
2.271	72.939	52.953	3.095	1.09

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

Magnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.039	58.445	0.592	0.074	1.07
0.083	58.964	1.285	0.119	1.39
0.124	59.425	1.902	0.159	1.57
0.165	59.914	2.556	0.199	1.66
0.196	60.285	3.050	0.215	1.82

Methylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.147	56.025	1.595	0.225	1.30
0.404	57.546	4.502	0.472	1.70
0.750	59.719	8.658	0.660	2.26
1.178	62.659	14.280	0.855	2.73
1.588	65.750	20.188	1.025	3.05
1.934	68.614	25.666	1.145	3.32
2.274	71.677	31.521	1.280	3.49
2.594	74.823	37.537	1.428	3.56
2.894	78.056	43.681	1.585	3.56
3.218	81.816	50.909	1.770	3.54

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

Mesitylmagnesium Bromide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.080	56.727	1.344	0.161	0.99
0.219	58.445	3.816	0.406	1.08
0.424	61.155	7.716	0.700	1.20
0.664	64.664	12.766	1.000	1.31
0.871	68.048	17.635	1.235	1.39
1.065	71.553	22.678	1.461	1.42
1.243	75.083	27.760	1.674	1.44
1.395	78.407	32.542	1.848	1.46
1.547	82.031	37.756	2.026	1.48
1.700	86.030	43.511	2.200	1.49

Magnesium Iodide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.050	60.725	1.061	0.096	1.05
0.126	62.613	2.772	0.194	1.30
0.225	65.262	5.173	0.263	1.72
0.355	68.481	8.090	0.312	2.16
0.458	72.438	11.676	0.344	2.66

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

Methylmagnesium Iodide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.114	58.123	1.592	0.189	1.20
0.301	60.002	4.340	0.400	1.50
0.572	62.954	8.658	0.596	1.91
0.892	66.836	14.334	0.756	2.31
1.168	70.587	19.820	0.878	2.63
1.420	74.398	25.393	0.982	2.85
1.646	78.191	30.941	1.082	3.00
1.846	81.883	36.341	1.170	3.10
2.037	85.736	41.976	1.262	3.17
2.218	89.748	47.843	1.357	3.20

Ethylmagnesium Iodide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.245	57.866	3.610	0.388	1.26
0.516	59.384	7.802	0.618	1.66
0.890	61.613	13.952	0.857	2.06
1.239	63.854	20.135	1.045	2.34
1.566	66.098	26.328	1.245	2.47
1.874	68.366	32.586	1.442	2.54
2.172	70.718	39.077	1.662	2.55
2.462	73.169	45.838	1.909	2.50
2.746	75.729	52.902	2.193	2.42

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

Phenylmagnesium Iodide

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.092	56.720	1.574	0.150	1.23
0.225	58.329	3.969	0.303	1.49
0.428	60.962	7.888	0.456	1.87
0.672	64.459	13.092	0.561	2.38
0.891	67.978	18.328	0.648	2.73
1.103	71.748	23.939	0.723	3.03
1.286	75.356	29.309	0.776	3.28
1.454	79.014	34.752	0.823	3.49
1.603	82.570	40.043	0.871	3.64
1.765	86.797	46.335	0.917	3.80

Dimethylmagnesium

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.024	57.540	0.177	0.043	1.11
0.087	60.083	0.670	0.126	1.39
0.275	69.283	2.451	0.338	1.62
0.358	74.243	3.411	0.427	1.67
0.499	84.666	5.429	0.568	1.75
0.607	94.859	7.403	0.683	1.76

Table 6. Association of Grignard and Related Magnesium Compounds in Diethyl Ether at Approximately 35°C (Continued).

Diethylmagnesium

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.072	56.374	0.641	0.139	1.05
0.230	57.409	2.064	0.397	1.16
0.484	59.171	4.485	0.773	1.24
0.797	61.488	7.672	1.200	1.30
1.079	63.744	10.773	1.560	1.35
1.352	66.080	13.984	1.893	1.39
1.605	68.414	17.192	2.202	1.41
1.860	70.932	20.654	2.508	1.42
2.108	73.576	24.289	2.830	1.42

Diphenylmagnesium

Concn., m	Solvent, g.	Solute, g.	ΔT, °C	Association, i
0.069	57.409	1.003	0.132	1.04
0.182	58.895	2.703	0.305	1.19
0.358	61.390	5.560	0.537	1.33
0.565	64.587	9.218	0.753	1.49
0.753	67.807	12.904	0.920	1.62
0.924	71.020	16.581	1.083	1.68
1.092	74.489	20.552	1.239	1.73
1.238	77.801	24.342	1.360	1.78
1.367	80.925	27.918	1.450	1.84
1.489	84.210	31.677	1.555	1.87

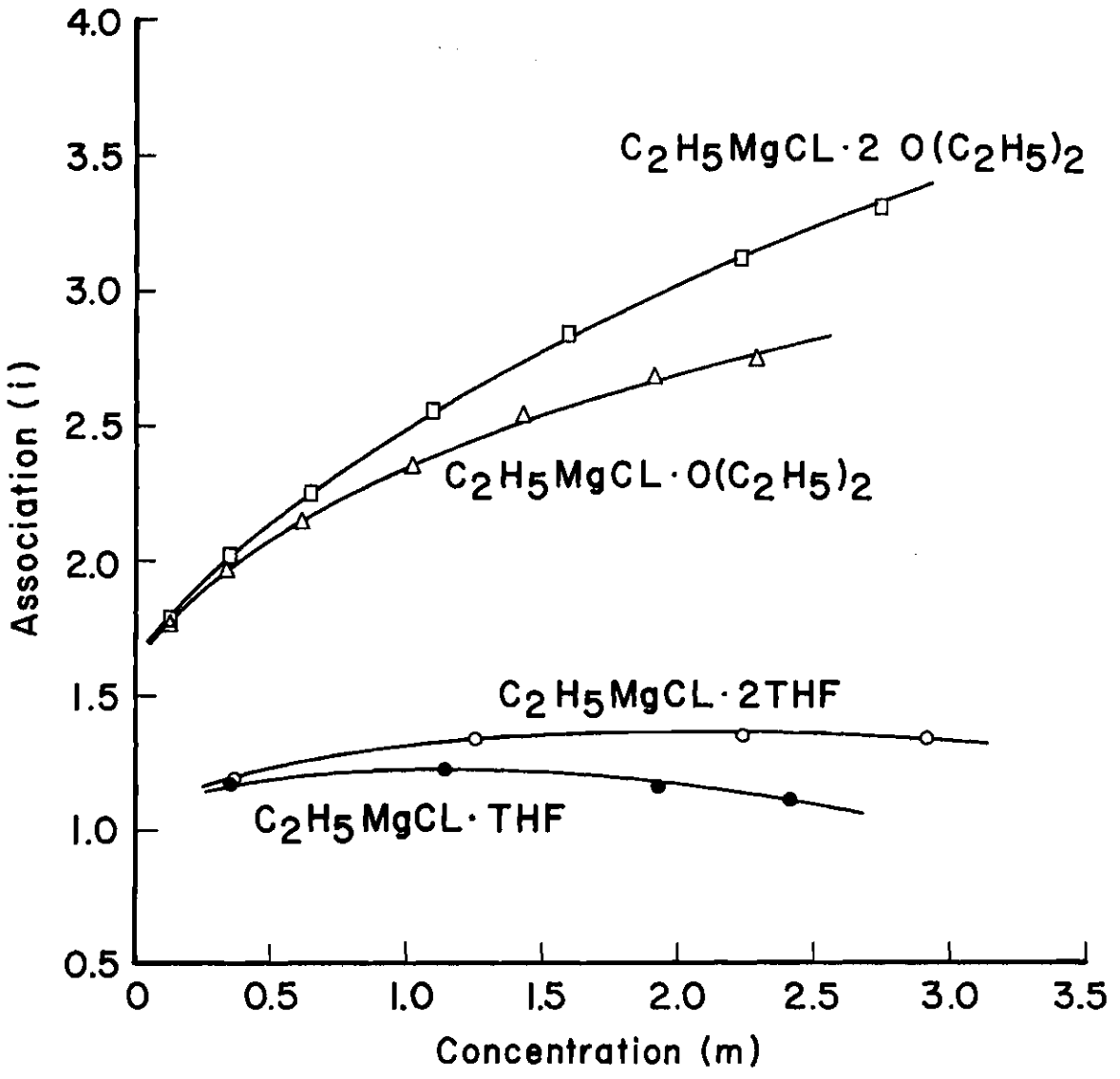


Figure 2. Demonstration of the Effect of Calculating Association of Grignard Compounds in Diethyl Ether and Tetrahydrofuran Based on Mono- or Disolvation.

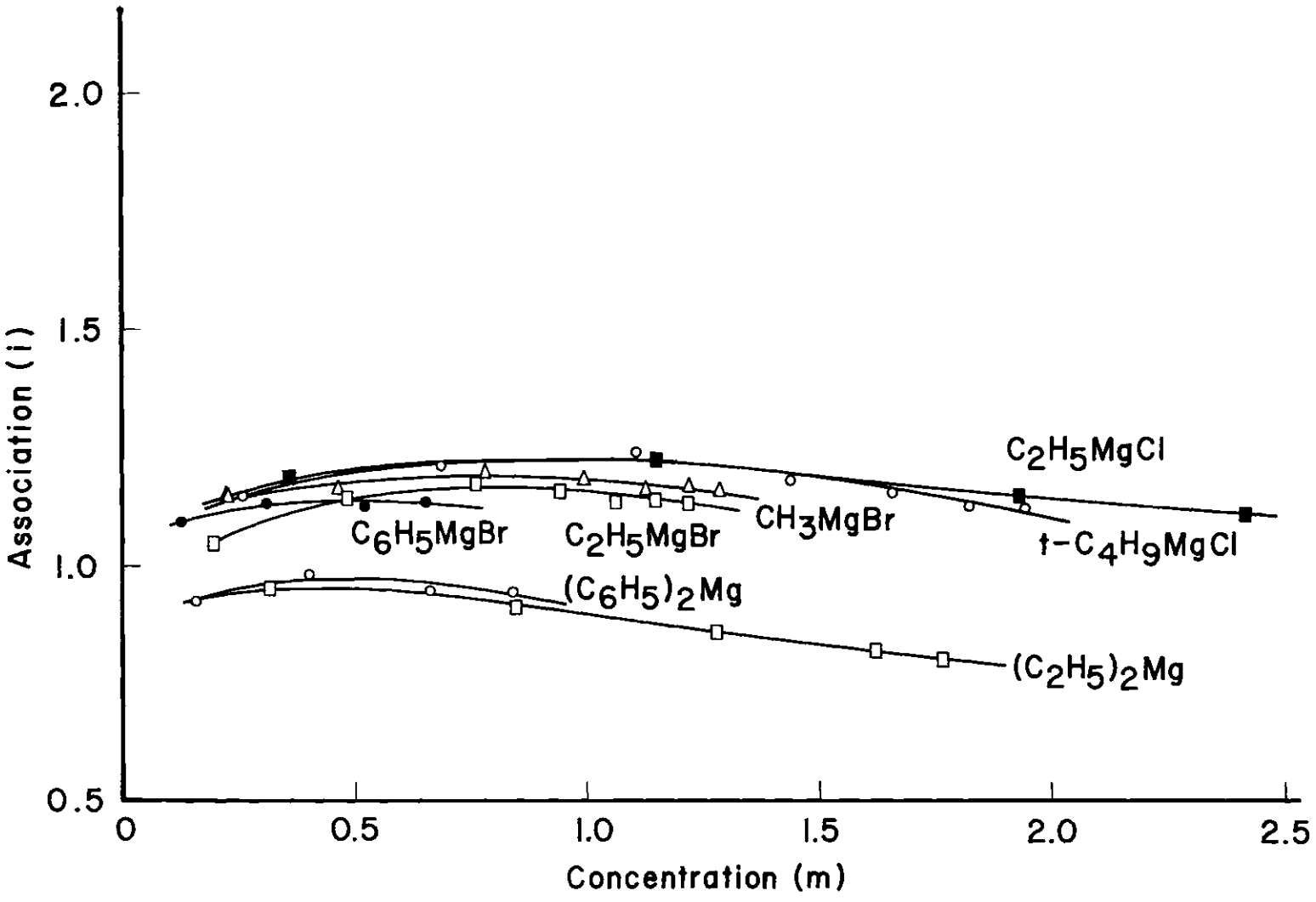


Figure 3. Association of Several Grignard Compounds in Tetrahydrofuran.

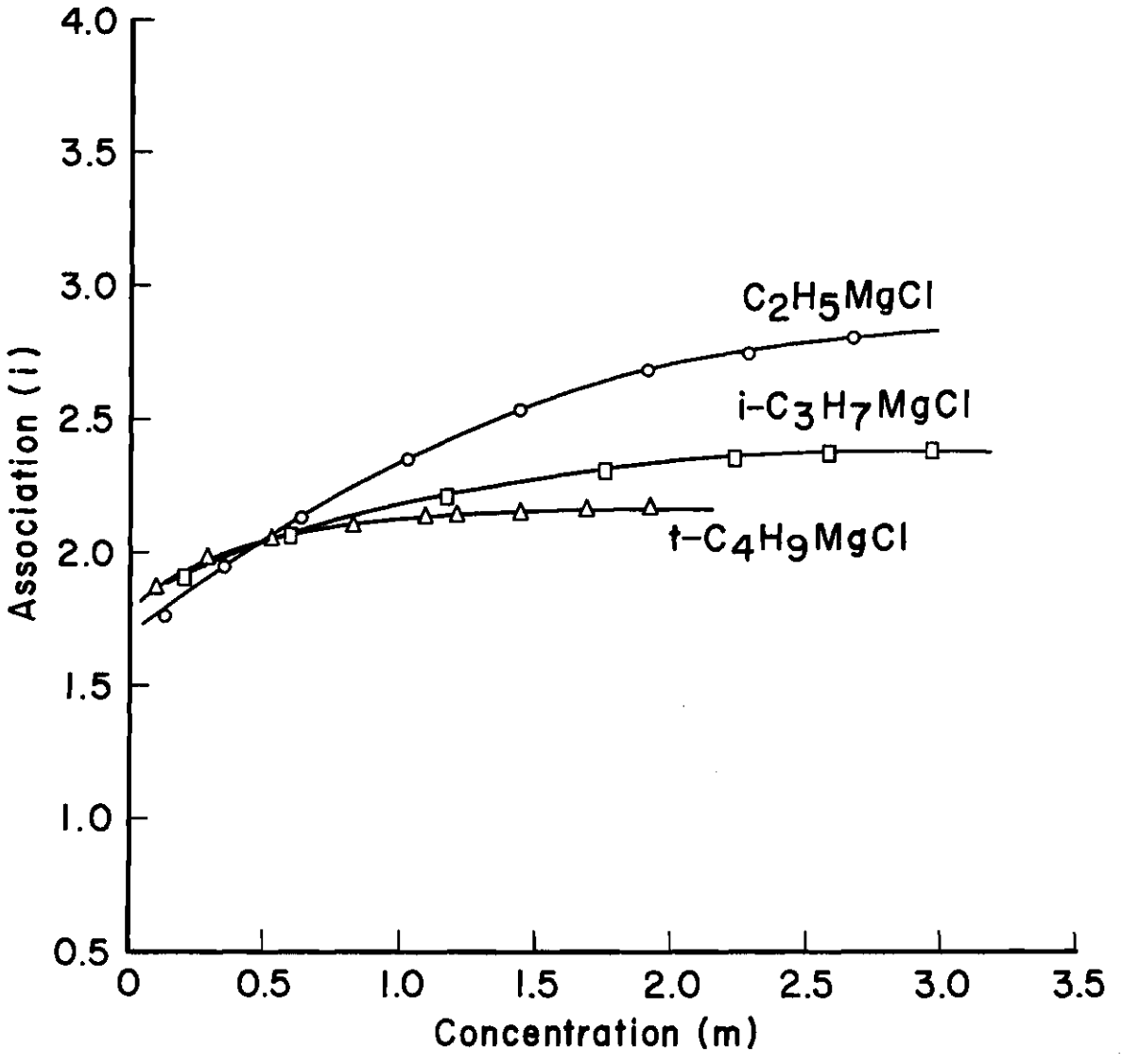


Figure 4. Association of Alkylmagnesium Chlorides in Diethyl Ether.

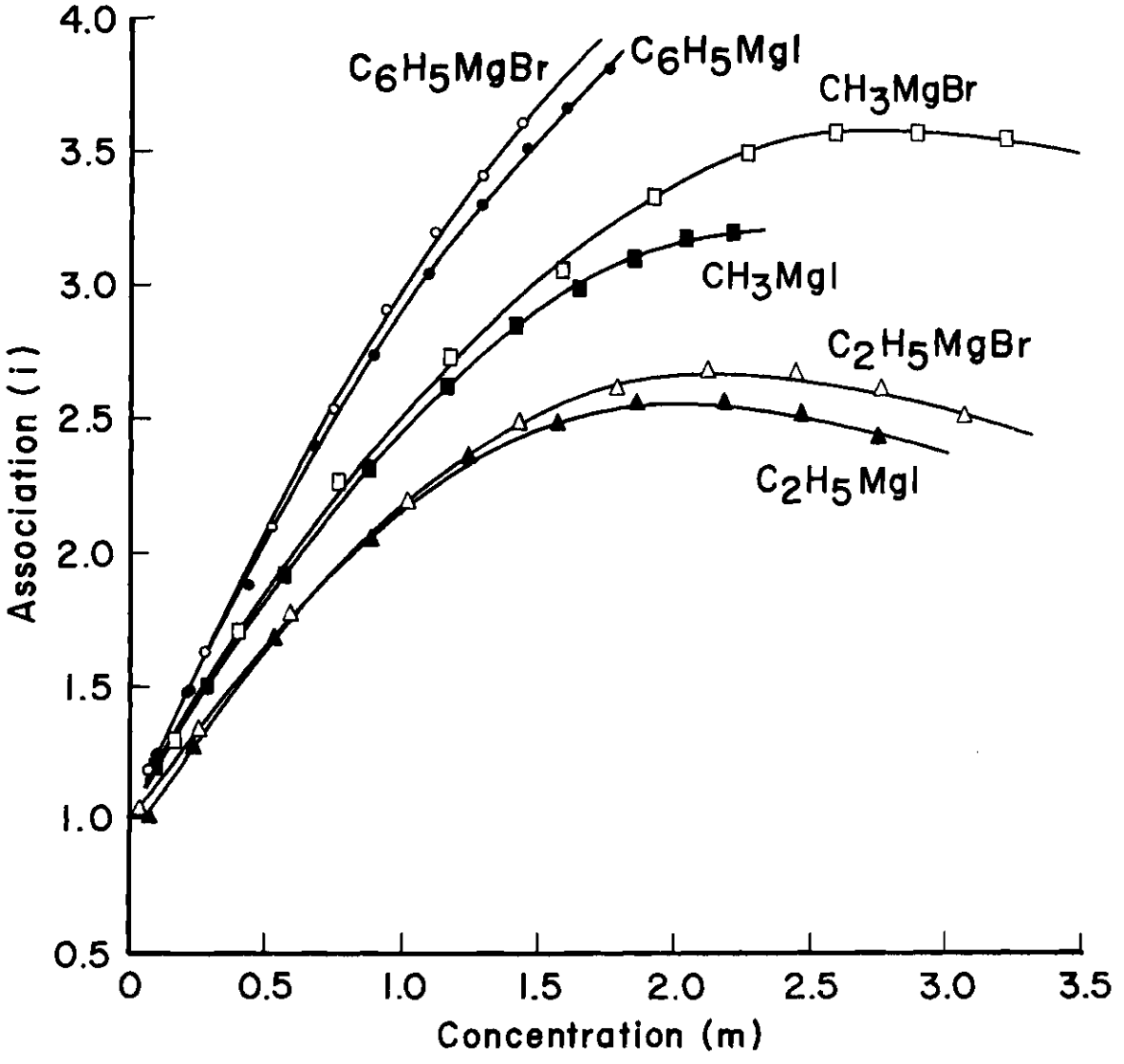


Figure 5. Association of Several Alkyl- and Arylmagnesium Bromides and Iodides in Diethyl Ether.

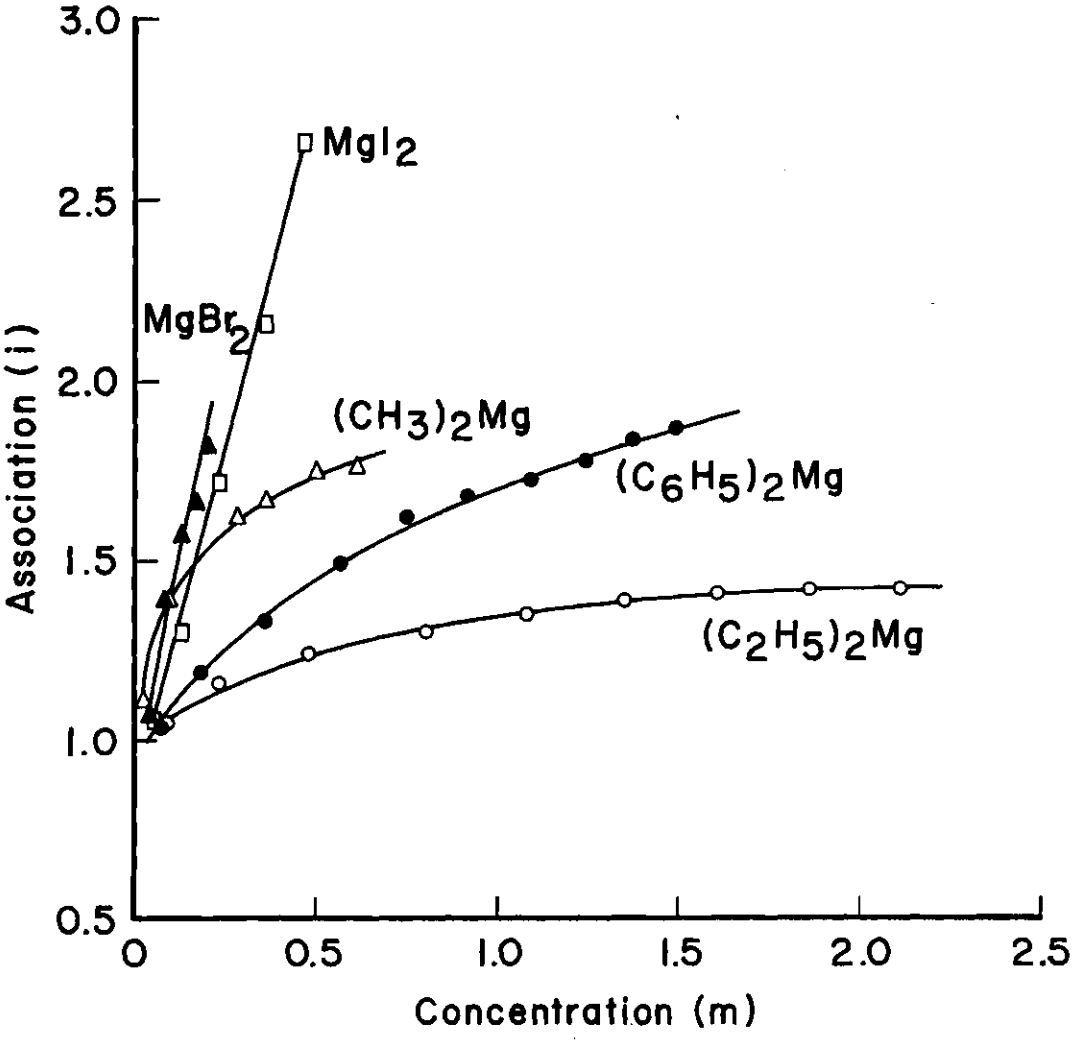


Figure 6. Association of Magnesium Halides and R_2Mg Compounds in Diethyl Ether.

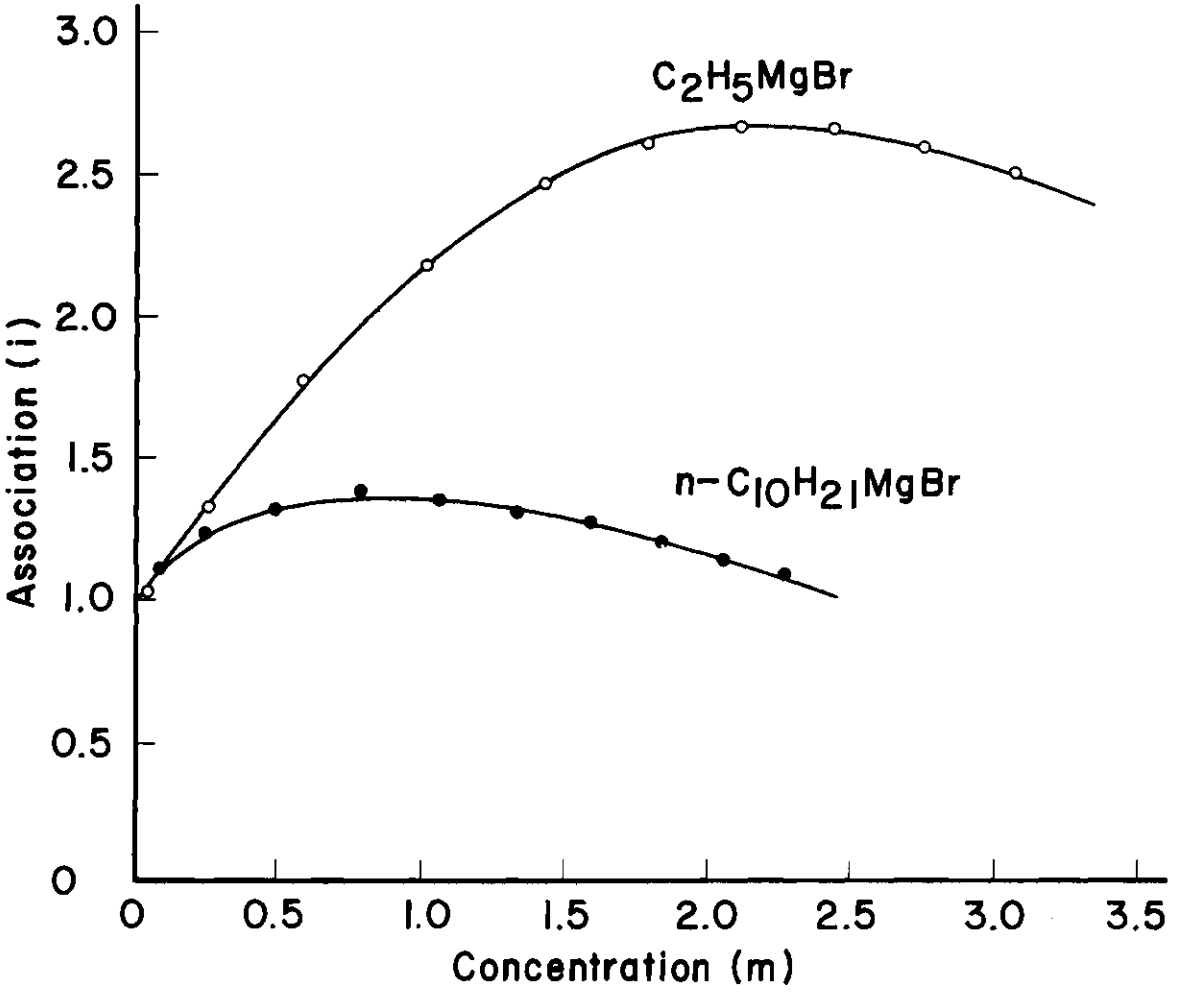


Figure 7. Association of Ethylmagnesium Bromide and n-Decylmagnesium Bromide in Diethyl Ether.

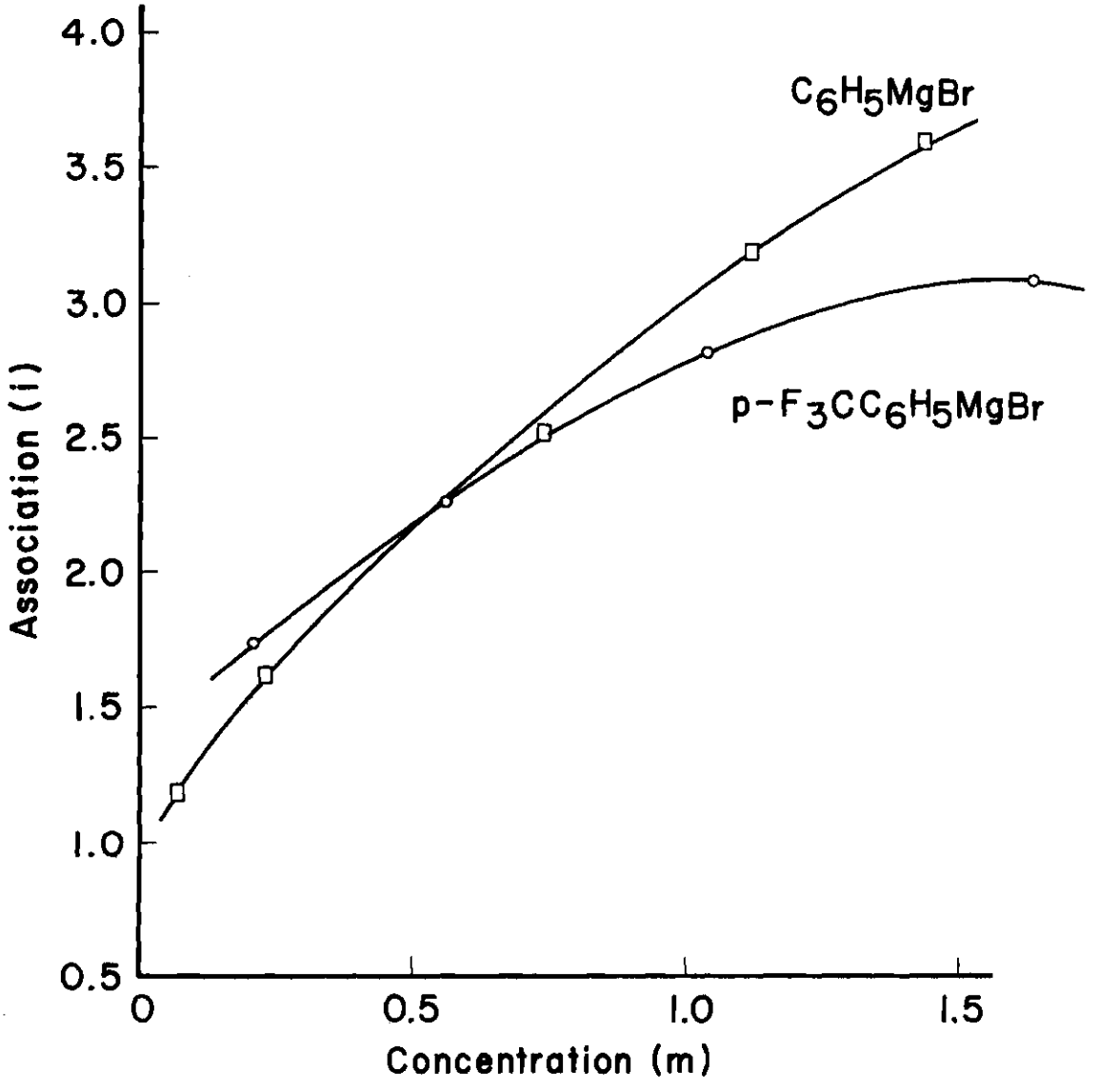


Figure 8. Association of p-Trifluoromethylphenyl- and Phenylmagnesium Bromide in Diethyl Ether.

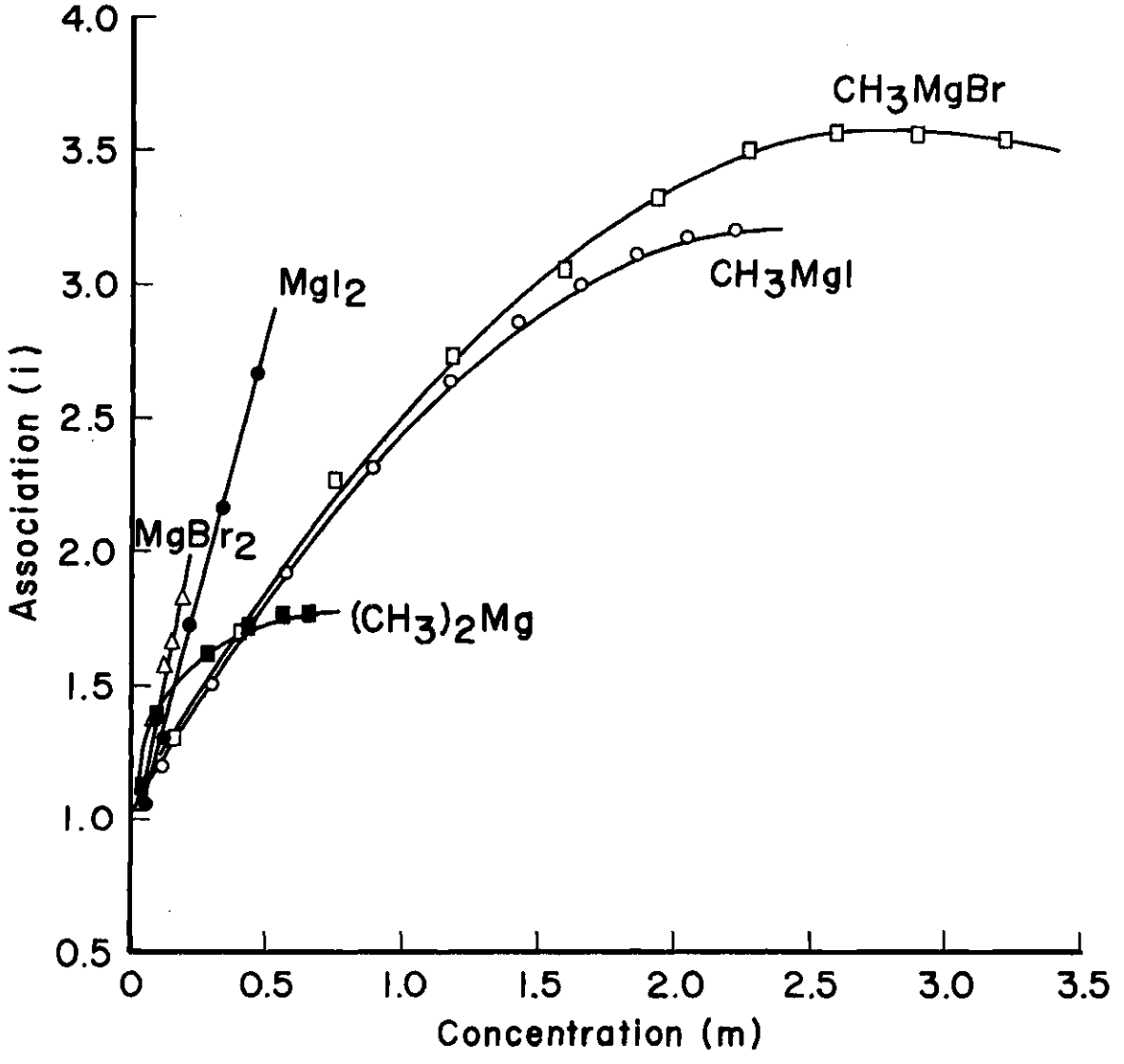


Figure 9. Association of Methyl Magnesium Compounds and Magnesium Halides in Diethyl Ether.

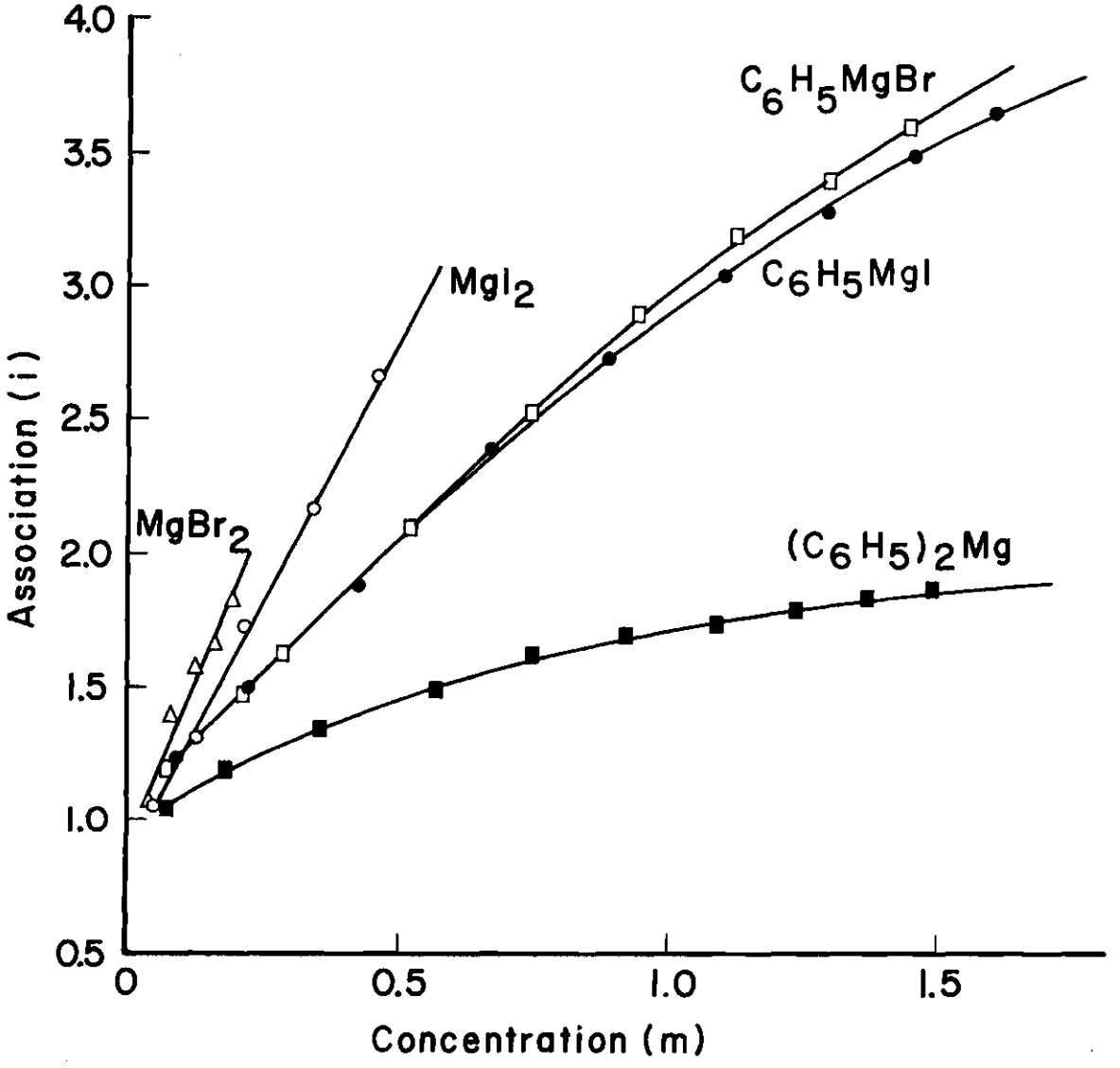


Figure 10. Association of Phenyl Magnesium Compounds and Magnesium Halides in Diethyl Ether.

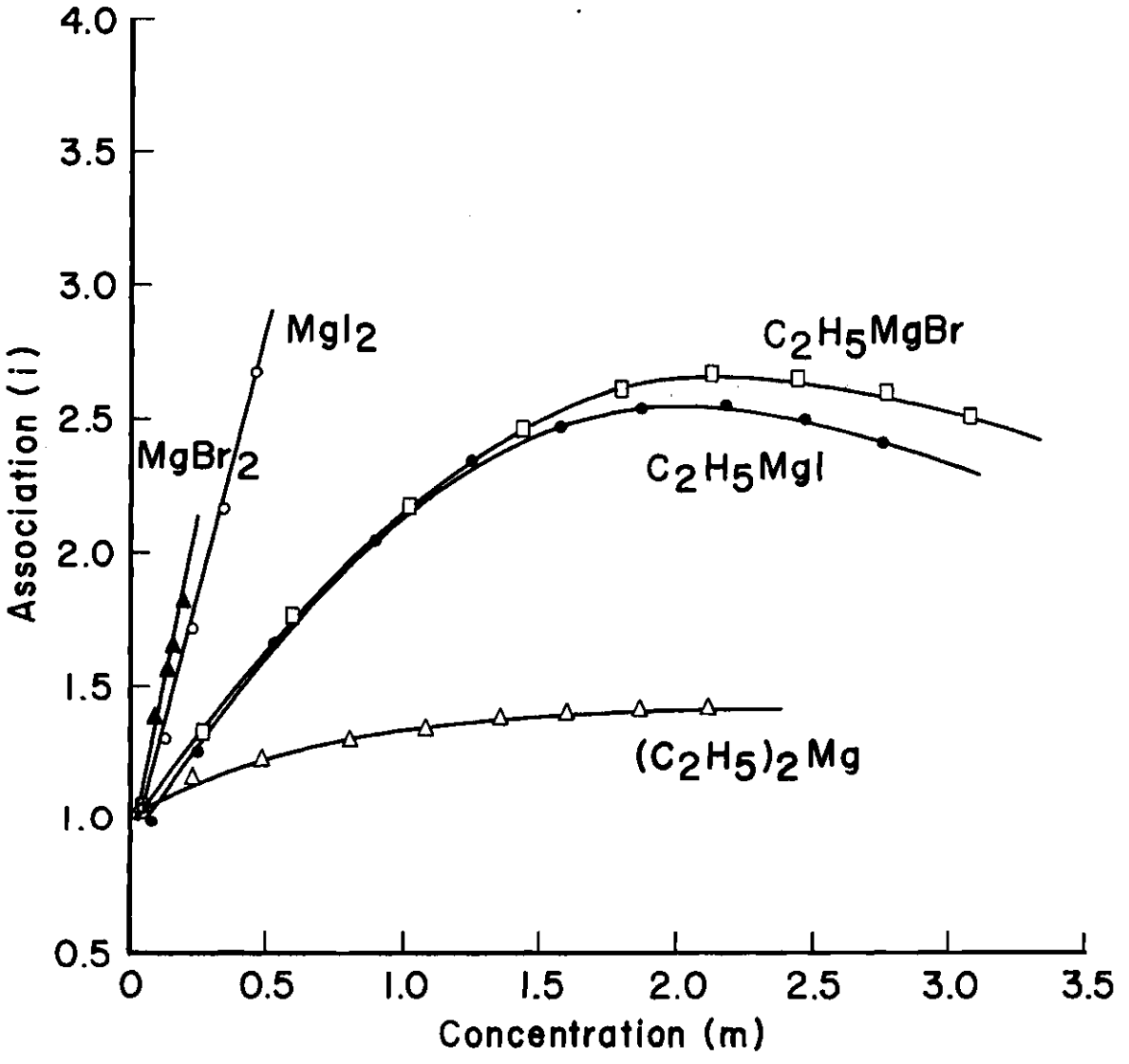


Figure 11. Association of Ethyl Magnesium Compounds and Magnesium Halides in Diethyl Ether.

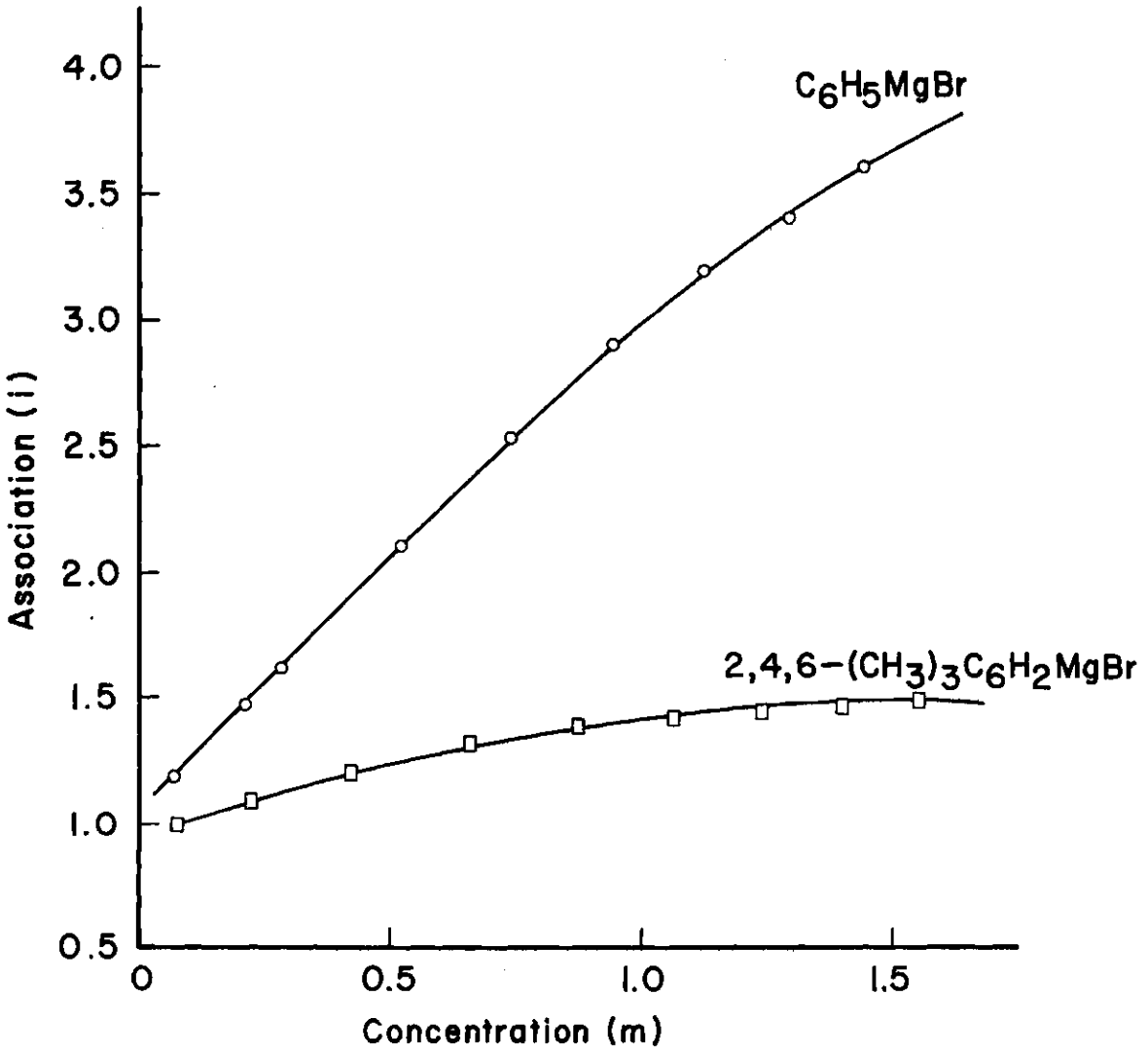


Figure 12. Comparison of the Association of Substituted vs Non-Substituted Arylmagnesium Bromides in Diethyl Ether.

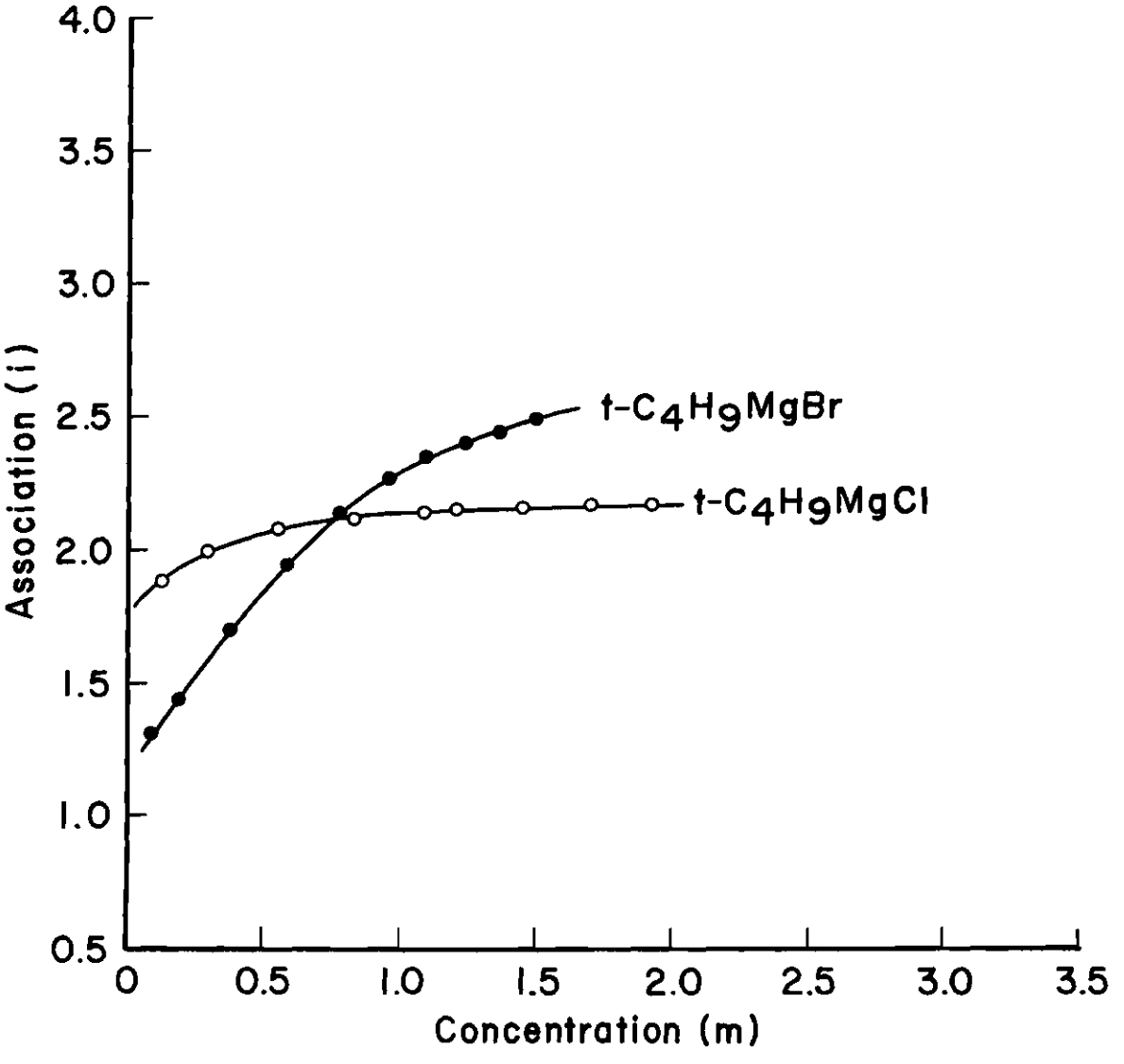


Figure 13. Demonstration of Importance of Halogen vs R Group in Determining the Form of Association in Diethyl Ether.

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PART III

REACTION OF METHYLMAGNESIUM BROMIDE WITH BENZOPHENONE IN DIETHYL ETHER. MECHANISMS AND PRODUCTS

CHAPTER I

INTRODUCTION

Background

After four decades of investigation there is still no agreement on the mechanism of the addition reaction of Grignard compounds with ketones to form tertiary alcohols. The history of this controversy is entertwined with the development of an understanding of the composition of the Grignard reagent (1). The result is that several mechanistic proposals have been advanced at three different periods during the last forty years.

Early Proposals for the Ketone Addition Reaction Mechanism

The first proposal to receive serious consideration in the early literature was that by Meisenheimer (2,3,4) who suggested the involvement of monomeric Grignard compound (Eq. 1).

$$G + K \rightleftarrows C \qquad (1)$$

$$C \rightarrow P$$

G = RMgX K = Ketone C = Complex P = Product

This was the first mechanism to envision the formation of a complex which subsequently rearranges to the observed carbinolate in the rate-controlling step.

A later proposal also postulated complex formation but, rather

than suggesting that the complex rearranges directly to product, Swain (5) suggested attack on the complex by a second molecule of monomeric Grignard reagent (Eq. 2).

$$G + K \rightleftarrows C \qquad (2)$$

$$C + G \rightarrow P + G$$

This proposal, based on product distribution studies with added magnesium bromide, was supported by Anteunis (6,7) who reported third-order kinetics for the reaction of methylmagnesium bromide and iodide with benzophenone and pinacolone, first-order in ketone and second-order in monomeric Grignard reagent.

The proposal of complex formation between Grignard and ketone in both mechanisms was based on color changes observed upon addition of the organomagnesium compounds to certain ketones and on reports that stable, ether-soluble one to one complexes between ketones and Grignard compounds had been isolated (8). Some of these complexes were later shown to be simply the magnesium halide carbinolates (9) and the concept of a stable one to one complex preceding the addition step was generally discounted in the subsequent formulation of mechanistic proposals.

Later Proposals for the Ketone Addition Reaction Mechanism

The next major development in the reaction mechanism story was a direct result of a now notorious report in 1957 (10) concerning the composition of the Grignard reagent. Based on an exchange study with magnesium isotopes, Dessy reported that magnesium alkyls and magnesium halides do not redistribute to alkylmagnesium halide and therefore suggested

that the Grignard compound is best represented as shown by Equation 3. Based on prior molecular weight studies in diethyl ether, the equilibrium was thought to lie almost entirely to the right.

$$R_2Mg + MgX_2 \rightleftarrows R_2Mg \cdot MgX_2 \qquad (3)$$

Soon after, three reports (11,12,13) were published depicting the mechanism of the addition reaction as going through a six-center transition state involving the newly proposed unsymmetrical dimer of the Grignard compound (Eq. 4).

$$2G \rightleftarrows G_2 \qquad (4)$$

$$K + G_2 \rightleftarrows C$$

$$C \rightarrow P$$

$$G_2 = R_2Mg \cdot MgX_2$$

This mechanism was based on finding second-order kinetics (11) for the first thirty per cent of the reaction between benzophenone and methylmagnesium bromide in tetrahydrofuran. Serious deviation from second-order kinetics was observed for the remainder of the reaction and overall the reaction was termed complex. In the same report the data presented by Anteunis in support of Swain's mechanism (Eq. 2) was criticized for several reasons, the most important being that a correct evaluation of the data does not indicate a third-order reaction. The mechanism shown in Equation 4 was also used to explain the results of various product distribution studies (12,13).

Current Proposals for the Ketone Addition Reaction Mechanism

Proponents of the various mechanisms offered no new data to support or refute any of the possibilities. Then, in 1963, a most interesting and important development occurred concerning the composition of the Grignard reagent. The presence of alkylmagnesium halide was detected in tetrahydrofuran (14) and a restudy of the exchange work (15) found, contrary to the earlier report, redistribution of magnesium alkyl and magnesium halide to alkylmagnesium halide. Now, the once discredited reaction mechanisms which formulated attack of the ketone by monomeric alkylmagnesium halide became credible once more.

The situation came full circle when the addition of methylmagnesium bromide to 2,4-dimethyl-4'-mercaptobenzophenone was interpreted (16) in terms of the original mechanism proposed by Meisenheimer (Eq. 1). This rather unusual ketone was used to shift the carbonyl absorbance to a longer wavelength since ethereal solutions of methylmagnesium bromide absorb strongly at shorter wavelengths. Thus, by following the reaction between the ketone and a large excess of Grignard compound directly by ultraviolet spectroscopy, it was found that both the carbonyl band and a longer wavelength absorption, attributed to a one-to-one ketone-Grignard complex, obeyed first-order kinetics in 0.04 to 0.30 M solution and disappeared at the same rate. Although the data were consistent with the mechanism up to a concentration of 0.30 M, serious deviation occurred at higher concentrations (up to 1.50 M).

Two alternative explanations were advanced to explain this deviation at higher concentrations. By including the adjustable parameter of a linear medium effect on the rate constant, the mechanism could be made

to fit the data at higher concentrations. Although this mathematical treatment is not without precedent, the weakness in this interpretation lies in the fact that even though the model with a linear medium effect can be made to fit the data, this does not mean that the model is valid. In other words, this treatment does not demonstrate the validity of the proposed mechanism in a positive way.

As noted earlier methylmagnesium bromide is associated at higher concentrations in diethyl ether. Therefore, the reactive Grignard species at higher concentrations need not necessarily be the same as that at lower concentrations. Smith and Su (16) recognized this and devised a scheme with a number of adjustable parameters to take association of the Grignard into account. The resulting mechanism approaches the one proposed earlier (Eq. 4) and, further, the constants that Smith and Su use suggest that the Grignard dimer (G_2) rather than the monomer is involved in most of the reaction (Eq. 5).

$$G_2 + K \rightleftharpoons C_2 \qquad (5)$$

$$C_2 \rightarrow P$$

Similar conclusions were reached for the reaction of n-butylmagnesium bromide with acetone in diethyl ether (17,18). By using infrared and calorimetric techniques, it was determined that rapid complex formation is followed by a first-order rearrangement of the complex to form product. However, the author (17,18) points out that, due to the experimental limitations, the data should be considered as only semiquantitative. Although these data (16,17,18) certainly are an important contribution to the reaction mechanism area, it is clear that the interpretation

of the data is open to question.

Soon after these reports, Ashby, Duke and Neumann (19,20) studied methylmagnesium bromide and benzophenone in diethyl ether. In order to avoid the complication of associated methylmagnesium bromide, the reaction was studied in solution dilute enough to insure that the Grignard was predominantly monomeric. Initially, the kinetics were studied for reactions in which the Grignard concentration was much greater than the ketone concentration. Since the Grignard is essentially opaque below 290 mμ, the higher absorbance of benzophenone (251 mμ) could not be used for following the reaction directly in the ultraviolet cell. Although benzophenone has an absorbance at 344 mμ where the Grignard is transparent, the extinction coefficient is quite small (Σ = 128). Thus, in order to use this absorbance, the solutions would have to be in the concentration range where the Grignard is associated. Therefore, analysis of the reaction solutions by ultraviolet spectroscopy demanded that the Grignard be destroyed before reading the absorbance of the ketone. The data, then, were obtained by quenching samples of the reaction mixture in aqueous ammonium chloride at different time intervals, filling the spectral cells with the ethereal portion of the quenched sample and following the diappearance of ketone at 251 mμ. The data for the high stoichiometry solutions indicated that the ketone was disappearing in a first-order fashion.

The data were tested for all of the mechanisms previously discussed by observing the dependence of the pseudo-first-order rate constant (k_{obs}) on Grignard concentration. The only mechanism that fit the data was one similar to that suggested by Swain (Eq. 6). When [G] was

plotted against $[G]^2/k_{obs}$ (Eq. 6), the points fell on a line with the required signs for the slope and intercept.

$$G + K \overset{K}{\rightleftarrows} C \qquad (6)$$

$$C + G \overset{k_3}{\rightarrow} P'$$

$$P' \rightleftarrows P + G$$

$$k_{obs} = \frac{k_3 K[G]^2}{1 + K[G]}$$

$$G = k_3 \frac{[G]^2}{k_{obs}} - \frac{1}{K}$$

Of course, when methylmagnesium bromide is in large excess, the final step in Equation 6, the complexation of the Grignard with product, can not be detected. However, this modification of the Swain mechanism was indicated by data from a study where the Grignard and ketone concentrations were comparable. The Swain mechanism (Eq. 2) proposes the immediate release of reactive Grignard during the rate-controlling step; limiting case of the modified Swain mechanism (Eq. 6) assumes that the Grignard remains complexed with the ketone. By using the equilibrium constant (1007) as given by the intercept of the line from the pseudo-first-order study, the rate constant for both mechanisms was calculated. Although detailed studies at low stoichiometry were not made, preliminary results were interpreted (19) as showing substantial agreement between

the rate constant calculated for the modified Swain mechanism and the rate constant calculated from the psudeo-first-order data.

There are several points about the methylmagnesium bromide- benzophenone systems that need clarification. Clearly, data from the pseudo-first-order study are not of the highest precision. Further, the criticism was voiced (21) that the equilibrium constant from extrapolation of the pseudo-first-order rate data is generally unreliable since a small change in the slope of the line will cause a significant difference in the intercept. As a matter of fact, the equilibrium constant reported by Smith and Su (16) (6.2 to 8.4) for their thiomethyl ketone is a good deal smaller than that reported (1007) for benzophenone (20). Therefore, in order to analyze the low stoichiometry data, a better value is needed for the equilibrium constant for methylmagnesium bromide-benzophenone complex formation. And, in order to realize this, better pseudo-first-order data on this system are needed. Further, the rate constants during a reaction at low stoichiometry show a tendency to decrease as the reaction progresses. Clearly, more work is needed with this system in order to establish the mechanism of the addition reaction.

The mechanism proposed by Smith and Su (Eq. 1) (16) seems to be in direct conflict with that proposed by Ashby, Duke and Neumann (19,20) (Eq. 6). It is not reasonable that, in dilute solutions, the reaction would involve complexation of the ketone by monomeric Grignard followed by attack on the complex by a second molecule of Grignard while at higher concentrations the reaction proceeds by complexation between ketone and monomeric Grignard followed by rearrangement of the complex to products. Actually, the latter mechanism might be expected to operate at lower con-

centrations while the former at higher concentrations. The mechanism involving reaction by the Grignard dimers (Eq. 5) is compatible with either mechanism proposed for the less concentrated solutions (Eq. 1 and 6).

Clearly, in spite of the determined effort by several research groups, the mechanism of the addition reaction is still a highly controversial topic. Although two main schools of thought have recently developed about the mechanism, neither group has been able to present irrefutable evidence to support their proposals.

Purpose

The kinetics of the reaction between methylmagnesium bromide and benzophenone in dilute diethyl ether solution was studied in an attempt to establish the mechanism of the addition reaction.

CHAPTER II

EXPERIMENTAL

Instrumentation and Apparatus

All ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer. A Zeiss PMQ II single beam spectrophotometer was employed for making the kinetic measurements, determining extinction coefficients and obtaining Beer's Law plots. Matched quartz cells (Beckman, 10.0 mm and Zeiss, 1.01 mm) were used for all ultraviolet measurements.

For the characterization of reaction products, a Perkin Elmer Model 237B grating infrared spectrophotometer was employed. Product distributions in the kinetic solutions were examined with a dual flame gas chromotograph (F&M Model 700).

A Sargent constant temperature water bath was used for controlling the temperature (±0.02°C) of the kinetic solutions; temperatures were monitored with a calibrated thermometer reading to 0.1°C with estimates to 0.02°C possible.

The reaction was timed with an electric stopwatch (Precision Scientific) reading to 0.1 second.

The kinetic flasks were fabricated by sealing a three-way Teflon stopcock to the top of a 100 ml heavy-walled glass bulb.

The syringes employed for transfer of the samples were calibrated with stainless steel needles.

An inert atmosphere box (Kewaunee Model 2C1020) equipped with a

recirculating system to remove moisture and oxygen (22) was used during the manipulation of reagents.

Chemicals

Benzophenone (Eastman's reagent) was distilled (88.0°C, 0.05 mm) twice under vacuum in a nitrogen system through an 18 inch vacuum-jacketed column packed with glass helices. A glpc analysis of diethyl ether solution revealed the material to be 99.95+% pure. Benzopinacol and benzohydrol were recrystallized from benzene; 1,1-diphenylethanol (Eastman reagent) was used without further purification.

Methyl bromide (Matheson, 99.5% purity) was dried and purified by passing through a 30 cm tube of NaOH pellets and then through a 70 cm tube of Linde 4A molecular sieve.

Triply sublimed magnesium (Dow), after washing with anhydrous diethyl ether, was dried and stored under nitrogen.

Diethyl ether (Fisher Anhydrous) was distilled under nitrogen from $LiAlH_4$ through a 60 cm distilling column packed with glass rings.

Analyses

Due to the dilute solutions used, the analysis of methylmagnesium bromide by simply withdrawing a sample for titration was impossible. The analysis was accomplished by preparing an excess of dilute methylmagnesium bromide in a tared flask. After withdrawing the amount needed for the kinetic study, the flask containing the remainder of the dilute solution was capped and reweighed. Then the total weight of solution in the flask was known and, from the density of diethyl ether at 25°C, the total volume was computed. At this point, the flask was opened and excess

0.01 N H_2SO_4 was added. After removing the ether under aspirator pressure on a steam bath, the excess H_2SO_4 was back-titrated with 0.01 N NaOH solution to a phenolphthalein end-point.

Benzophenone concentrations in the kinetic solutions were determined by ultraviolet spectroscopy at 251.0 mμ ($\Sigma = 1.80 \times 10^4$) in quartz cells with tightly fitting ground glass and Teflon stoppers.

Benzophenone, 1,1-diphenylethanol, 1,1-diphenylethylene (the dehydration product of 1,1-diphenylethanol) and benzhydrol were all successfully analyzed by glpc using stainless steel columns packed with Chromosorb W coated with 10% Carbowax 20M.

However, all attempts to analyze benzopinacol by glpc failed. The problem with benzopinacol is two-fold. First, the compound decomposes thermally (23) to benzophenone and benzhydrol at 180°C. However, the alcohols present in the reaction mixtures either failed to emerge from the columns at temperatures below 180°C or emerged without separation. The analysis was attempted with stainless steel columns packed with 2% and 10% Carbowax 20M on Chromosorb W; 10% SE30 on Chromosorb S; Poly-pak 1; and 10% Polyphenol Gaschrom Q. Although 2% and 6% Ucon Polar 50HB5100 on Gaschrom Q were the only columns to separate all of the compounds at low injection port and oven temperatures (115°), benzopinacol still decomposed. The stainless steel columns (24,25) might contribute to the decomposition of benzopinacol but this was not established.

Attempts to analyze benzopinacol by first converting it to benzopinacolone with strong acid and then analyzing by glpc or ultraviolet spectroscopy also failed. With glpc, benzopinacolone either failed to emerge from the columns tested (see above) or appeared without separation from the other reaction products. Under conditions that convert benzo-

pinacol to benzopinacolone, 1,1-diphenylethanol dehydrates to 1,1-diphenylethylene which completely masks the absorbance of benzopinacolone in the ultraviolet spectrum.

Preparations and Procedures

General Procedures

The great difficulties encountered when working with such dilute Grignard solutions (highest concentration was 8×10^{-3} M) can hardly be overemphasized. Techniques that are satisfactory for the preparation of clear concentrated solutions fail for these dilute solutions. Many methods for drying the equipment such as flaming under a flow of nitrogen were tried but in every case the dilute methylmagnesium bromide solutions hydrolyzed as evidenced by a faintly blue solution. This blue cast is due to a finely divided solid that remains suspended in solution for several hours. Perhaps in the more concentrated solutions the solubility of the alkoxide impurities is increased by association with the methylmagnesium bromide. Apparently, in the dilute solutions, the alkoxides fail to associate with the monomeric Grignard and simply precipitate from solution.

Considerable time was spent in developing the following procedures and it is imperative that the steps outlined are followed. When this is done, absolutely clear diethyl ether solutions of methylmagnesium bromide at a concentration of 5×10^{-4} M can be prepared.

Whenever diethyl ether was distilled, an initial portion was collected in a small receiver and discarded. This rinsed the internal part of the still that could not be dried by external heating. The main receiver was then placed on the still and, after isolating the portion of

the apparatus containing the ether still by closing the stopcocks, a vacuum of 0.05 mm was applied. The flask was gently flamed and allowed to cool before readmitting a nitrogen atmosphere. This step was then repeated. The filled flask was removed from the still under a heavy nitrogen flow and capped for transfer to the dry box.

All of the solutions, under a flow of prepurified nitrogen in the dry box were sampled via syringe through three-way Teflon stopcocks.

The kinetic flasks, syringes and needles were rinsed with ether, heated over a burner flame and then placed into the entry port which was subsequently evacuated to a pressure of 0.25 mm of Hg. After filling the chamber with nitrogen, the equipment was transferred into the dry box and assembled after a thorough purge with a stream of prepurified nitrogen that had been subjected to additional drying with a 90 cm tube of Linde 4A Molecular Sieve.

Preparation of Methylmagnesium Bromide

The preliminary drying steps were the same as those described for the distillation of diethyl ether. The ether still was connected to a Dry Ice-acetone condenser and a 500 ml round-bottom one-neck flask containing triply sublimed magnesium (19.4 g, 0.8 g-atom) and a stirring bar was connected to the bottom of the condenser. The condenser was charged with Dry Ice and, after distilling approximately 50 ml ether into the reaction flask, methyl bromide was introduced through a side arm near the base of the condenser. After the reaction had initiated, as evidenced by bubbling and heat release, stirring was started. The diethyl ether and methyl bromide were added at a rate to maintain gentle boiling of the solution without external heating. The methyl bromide was added until

approximately one-half of the magnesium was consumed, and the distillation of the ether was continued until the flask held approximately 400 ml solution. Stirring was continued until the reaction had ceased and the flask had cooled to room temperature. The reaction flask was removed from the assembly under a heavy flow of nitrogen, capped, and placed into the dry box.

Dilute solutions of methylmagnesium bromide were prepared in the dry box under prepurified nitrogen by adding a portion of the concentrated solution via syringe to a one-neck round-bottom flask containing freshly distilled diethyl ether. By observing the precautions outlined above, prefectly clear solutions of methylmagnesium bromide in the concentration range of 5×10^{-4} M were prepared.

Preparation of Benzophenone Solutions

The solutions were prepared by adding weighed quanitities of benzophenone to tinted volumetric flasks in the dry box. After dissolving in diethyl ether the concentrations were checked by ultraviolet analysis. It was found convenient, for several reasons, to work with a benzophenone solution in the concentration range of 0.05 M. This concentration allowed the addition of 0.04 to 0.16 ml samples to 70 ml of Grignard solution in the kinetics flask to obtain initial absorbancies in the range of 0.4 to 1.2. The samples were small enough to allow rapid addition when the reaction was initiated and small enough to have a negligible effect through dilution on the Grignard concentration. Finally, since the viscosity of 0.05 M benzophenone solutions is not very different than that of pure diethyl ether, no concentration layers were formed. This made for easy mixing after initiation by simply swirling the solution.

Extinction Coefficients

The extinction coefficients of benzophenone ($\Sigma = 1.80 \pm 0.01 \times 10^4$) and 1,1-diphenylethanol ($\Sigma = 349 \pm 4$) were determined at several concentrations in diethyl ether at 251 mμ. The 1.01 mm cells were used so that the largest possible samples of benzophenone could be employed (0.01 to 0.04 g) in a reasonable amount of diethyl ether (approximately 250 ml). Benzophenone was more difficult to work with than 1,1-diphenylethanol since the high extinction coefficient severely limited the quantity of material that could be used.

The samples were first weighed in a tared flask capped with an ungreased glass stopper. Then diethyl ether was added and the flask reweighed. The stopper was immediately removed and replaced with a lightly greased joint with a stopcock. This arrangement allowed several samples to be withdrawn through the stopcock without ether loss. The solutions obeyed Beer's Law over a concentration range of 1.9 to 6.8×10^{-4} M.

Quenching Solutions

Several solutions were investigated for use as quenching agents for the kinetics samples. Two problems had to be considered. First, the solution must be capable of complete and rapid hydrolysis of the methylmagnesium bromide in the kinetics samples and complete dissolution of the magnesium salts. Second, the quenching solutions must not affect the ketone concentration in the samples. Ammonium chloride solutions were used previously (20) but two problems were encountered with this method. First, the ammonium salts taken into the ether layer by dissolved water precipitated on the windows of the quartz cells. This caused a severe drift in the absorbance readings. Second, the absorbancies of

unquenched standard benzophenone solutions were considerably lower than the absorbancies of the quenched solutions.

The increased absorbance readings were also found when 10% H_2SO_4 was used for the quenching solutions. However, the absorbance readings did not drift as they did with 10% NH_4Cl. It was felt that the high readings in the quenched solutions were due to ether dissolving in the water layer. Attempts to prevent this by quenching at 0°C or salting out the quenched solutions failed. Rather than trying to prevent ether from dissolving in the water layer, it was decided to saturate the 10% H_2SO_4 with ether prior to quenching. A seperatory funnel with a Teflon stopcock to avoid contamination by grease was used for this purpose. The method worked perfectly and the absorbance of several quenched solutions matched exactly the absorbance of the unquenched standard sample. The absorbancies of standard samples of the products were also unchanged by this quenching method.

Kinetic Studies

A 70.0 ml portion of the dilute methylmagnesium bromide was transferred from the dilution flask via syringe to the reaction flask under a flow of prepurified nitrogen in the dry box. The stopcock on the reaction flask was closed and the unused portion of the dilute methylmagnesium bromide was capped and retained for analysis. The flasks were removed from the dry box along with a syringe containing benzophenone solution.

Ten syringes with stainless steel needles were rinsed with ether and after flaming, were purged with nitrogen by drawing the gas into the barrel through the needle several times. The purging step was repeated

after the syringes had cooled and approximately four ml of nitrogen was retained in the barrel of the syringe. Ten test tubes with ground glass stoppers were rinsed with ether and flamed. A 10% H_2SO_4 solution was saturated with ether in a seperatory funnel equipped with a Teflon stopcock and approximately five ml of this solution was transferred to the cool test tubes.

A nitrogen line was hooked to the stopcock at the top of the reaction flask after securely clamping the flask in a constant temperature bath set at 25.0°C. After turning the stopcock in a manner to bypass the opening to the solution, the line and stopcock were purged with nitrogen. The stopcock was then turned to accept a syringe needle from the top with a nitrogen flow from the side. The desired portion of benzophenone was added from a syringe and the timer started. The nitrogen remaining in the sampling syringes was discharged through the needle into the nitrogen flow from the reaction flask. Immediately the needle was inserted into the reaction solution through the three-way Teflon stopcock. A sample was withdrawn and quenched in the test tubes containing the ether-saturated 10% H_2SO_4 solution. The tubes were capped immediately after quenching to prevent evaporation of the ether. The time at which the plunger reached midpoint was recorded as the reaction time.

After taking ten samples at appropriate periods of time, the amount of unreacted ketone in each sample was determined at 251.0 mμ by filling quartz cells via syringe with the ether layers of the quenched solutions. Hydrolyzed methylmagnesium bromide of the same concentration as the reaction solution was used in the reference cell. Some of the samples were also analyzed by glpc. A sample was removed after a couple

of days for an infinity reading and glpc analysis.

Product Studies

The procedure described here has been used for similar product analyses (16,21). Diethyl ether solutions of methylmagnesium bromide (0.052 mol) and benzophenone (0.001 mol) were mixed in a 250 ml flask and allowed to react overnight in the dry box. The solution was hydrolyzed with water and just enough 10% H_2SO_4 to dissolve the magnesium salts. The ether portion was washed with two portions each of saturated Na_2CO_3 solution and distilled water. The ether was removed on a steam cone at water aspirator pressure and the residue was dissolved in 50 ml benzene. After adding 0.098 g p-toluenesulfonic acid, the solution was boiled and the water-benzene azeotrope collected with a Dean-Stark head. After removing the benzene on a steam cone at water aspirator pressure, the residue was redissolved in ether and washed twice with Na_2CO_3 solution and then distilled water. After drying the ether layer with $MgSO_4$ overnight, the ether was removed and the residue dried on a vacuum manifold for two hours. An authentic sample of 1,1-diphenylethanol was treated in the same manner as the reaction product. Both products were examined gy glpc and infrared spectrophotometry.

Some of the reaction solutions directly from the kinetic studies were examined for product distribution. This was accomplished by concentrating the quenched samples under a stream of nitrogen and analyzing the solution without further treatment. The analyses were carried out with glpc using stainless steel columns packed with 10% Carbowax 20M on Chromosorb W.

Due to the number and variety of products in solution, a satisfactory internal standard could not be found. Therefore, in order to check the yield, samples were withdrawn early in the reaction, the absorbance of the benzophenone was determined, and the solutions were analyzed by glpc. Since it had been determined earlier that the compounds have the same peak area for a fixed number of moles, the molarity of the solutions with respect to each compound could be calculated by comparing the relative areas directly with the area from the known amount of benzophenone. A number of determinations indicated an overall yield of 100±5%. The uncertainty is probably due to accumulated inaccuracies in computing the areas of the large number of peaks and the regeneration of benzophenone in the later fractions by decomposition of benzopinacol in the gas chromatograph as discussed later. Nevertheless, it seems fairly certain that the sum of the areas closely represents the total reaction product and it was on this basis that the per cent yields shown in Tables 4 and 5 were calculated.

CHAPTER III

RESULTS AND DISCUSSION

Studies of the Disappearance of Ketone

Attempted Use of Individual Reaction Flasks

Initially, many attempts were made to obtain data on the reaction of a large excess of methylmagnesium bromide with benzophenone in diethyl ether using the same procedure employed in the earlier study (2) with this system. An improvement over the precision of the available data was hoped for since this would allow a more precise check on the previous mechanistic conclusions (19,20).

Use was made of several 25 ml volumetric flasks, each equipped with a downward tilting side arm between the graduation mark and the stopper. The side arm was loaded with benzophenone, and methylmagnesium bromide was placed into the lower portion of the flasks. The reaction was started by inverting the flasks to mix the Grignard and ketone solutions. Each piece of datum then was obtained from a separate reaction solution by timing the reaction in each flask from initiation to quenching. All of the reactions were carried out with 7.5×10^{-3} M methylmagnesium bromide and 5×10^{-5} M benzophenone, resulting in a ratio of 150 to 1.

Although the experimental method seems straightforward, a most unusual series of events transpired during the course of the study. When the reaction flasks were loaded in the dry box atmosphere after purging with prepurified nitrogen, the data for the disappearance of benzophenone displayed some small scatter (A in Figure 1). At that time the

flasks were capped with lightly greased ground glass stoppers. Since grease interferes with the ketone absorbance at 251 mμ, the scatter was attributed to a small amount of grease dissolved in the diethyl ether. An attempt was then made to find a cap that could be used without grease; polyethylene stoppers met this requirement.

A reaction duplicating the conditions used with the greased ground glass stoppers was examined and the data scatter was worse (B in Figure 1). Two things suggested that this was due to leakage around the new caps. First, the fact that the data were scattered indicated that varying amounts of Grignard was being destroyed in each flask. Second, the fact that the absorbance values were generally higher throughout the reaction, although the concentrations of the reactants were the same as used previously, pointed to loss of active Grignard.

The desirability of using the polyethylene caps which would eliminate contamination by grease was so great that an extensive series of adjustments in the methods for handling the equipment and reactants was undertaken. The modifications included fire polishing the ground glass joints on the reaction flasks, sampling the reactants under a flow of prepurified nitrogen in the dry box, greasing the outer ring on the polyethylene caps (two inner rings prevented contact between the grease and ether), varying the amount of time the equipment was subjected to vacuum in the entry port and varying the order in which the flasks were loaded with reactants and purged with prepurified nitrogen. With each additional modificiation, kinetic data from the subsequent reaction remained seriously scattered.

Finally, after many changes, the ultimate precautions for elimi-

nating contamination by moisture and oxygen were realized. The equipment was flamed and placed in the dry box entry port which was then evacuated to 0.25 mm Hg. This pressure was maintained for twelve hours. The port was refilled with nitrogen and reevacuated to the same pressure for an additional four hours. Once inside the dry box, the equipment was purged with prepurified nitrogen. The reaction flasks were loaded through an opening in a cap that held a tube from the prepurified nitrogen line. The reaction flasks, which were continually swept with prepurified nitrogen, were loaded with the reactants which were also continously swept with prepurified nitrogen in the dry box. With these precautions, the benzophenone gave little indication of reaction (C in Figure 1) in three separate and independent experiments. The reason for this behavior is not known. However, if one were asked to speculate, it would be tempting to suggest that the presence of either water or, more likely, oxygen is a necessary condition to achieve reaction between methylmagnesium bromide and benzophenone.

Regardless of the specific agent (if any) responsible for the reaction, it remained imperative to find an experimental method with which reproducible kinetic data could be obtained. Only then could the various factors leading to reaction between the Grignard and the ketone be studied. This was realized by the use of the kinetic method previously described (Experimental Section) where one reaction solution was sampled at appropriate intervals for each complete kinetic run.

Use of Sampling Technique

The reaction of a large excess of methylmagnesium bromide with benzophenone in diethyl ether was reexamined. A typical set of data is

shown in Figure 2 where A_c, the absorbance corrected for product formation, is plotted against time on semi-log paper. More will be said about the absorbance correction later. Although the data show a good first order disappearance of ketone for most of the reaction, the absorbance values are high in the early part of the reaction. This behavior is probably related to the observation in the previous study (20) that the extrapolated A_o fell below the calculated value; the kinetic method used in the earlier study (small flask technique) allowed the accurate calculation of A_o. The sampling technique used in this study does not permit an accurate value of the initial ketone concentration to be calculated and depends solely on the extrapolated value for A_o.

When the initial concentration of methylmagnesium bromide was held constant and four different ketone concentrations were used (Tables 1 and 2), the rate constant changed (Table 3). This behavior is shown in Figure 3 where the values for the rate constant calculated from the slope of the lines in the first order plots (Figure 2) are plotted against the extrapolated values for the initial ketone concentrations. The constancy of the Grignard concentration was assured by filling four reaction flasks from the same Grignard preparation and storing the sealed flasks in the dry box away from light. The reactions were run in a staggered fashion to demonstrate that any difference in the rate constants was not simply a reflection of Grignard deactivation by moisture or oxygen during storage. Clearly, the ketone is not disappearing in a purely first-order fashion since the rate constant should be independent of the initial ketone concentration. The relationship between this behavior and the initial curvature observed in the pseudo-first-order plots has not been established.

Studies of the Formation of Products

Product Study

Initially, a product study independent of the kinetic solutions was conducted. An infrared spectrum of the dehydrated reaction product was very similar to the spectrum of the material obtained by dehydrating an authentic sample of 1,1-diphenylethanol. A glpc analysis failed to reveal any volatile impurities. However, an internal standard could not be used to check the yield of reaction product since the amount of volatile reaction product decreased rapidly with time. The material changed from a glass to a gritty solid and this was tentatively attributed to polymerization of the olefin.

Products in the Kinetic Solutions

Although the product study gave little indication of appreciable side reaction, the values for the pseudo-first-order rate constant suggested that an examination of the kinetic solutions directly for products was in order. The reaction solutions were so dilute that isolation of the products was impossible, but examination by glpc indicated that a significant quantity of ketone was being diverted to some reaction other than addition (Table 4). Benzophenone, 1,1-diphenylethanol, 1,1-diphenylethylene (from the dehydration of 1,1-diphenylethanol in the gas chromatograph) and benzhydrol were identified by their glpc retention times. A very small amount of another product was indicated in some cases but could not be identified. Benzophenone was not present in the kinetic solutions before the glpc analysis as indicated by the ultraviolet spectrum of a hydrolyzed sample of the reaction solution. A search of the literature revealed some generally overlooked reports (26,

27,28) on the formation of pinacols in the reaction of Grignard compounds with ketones. Analysis of an authentic sample of benzopinacol under the glpc conditions used for the reaction solutions showed that the products were indeed benzophenone and benzhydrol.

However, the decomposition is not straightforward in that benzophenone and benzhydrol are not formed in equivalent amounts. The decomposition of benzopinacol seems to be somewhat random in that the benzophenone to benzhydrol ratio is 15 to 1 in standard diethyl ether solution but, when the solution is treated with 10% H_2SO_4, the ratio changes to 7 to 1. However, in every case benzophenone was formed in large excess. Although there is a marked variation in the benzophenone to benzhydrol ratio from the different reaction solutions (Table 4) which might be attributed to random decomposition, in most cases there is significantly more benzhydrol than benzophenone. Therefore, it is possible that the decomposition of benzopinacol is not the only source of benzhydrol.

Although it is not known definitely, it appears very likely that the side reaction is related to the behavior observed for the pseudo-first-order rate constant (Table 3 and Figure 3). The reason for this uncertainty lies with the difficulties encountered in trying to analyze the solutions for benzopinacol. Repeated attempts to observe benzopinacol directly, rather than indirectly as by the decomposition products failed.

Not knowing if benzhydrol arises from a source other than benzopinacol makes interpretation of kinetic data gathered by glpc difficult. Since benzophenone is the other product of the decomposition and since unreacted benzophenone is also present during the reaction, the only

measure of the extent of side product formation is by the amount of benzhydrol formed in the decomposition process. Nevertheless, one set of data was gathered by glpc and the results are shown in Table 5. There does appear to be some constancy of the 1,1-diphenylethanol:benzhydrol ratio throughout the reaction which would indicate that the addition reaction and the side reaction are related in some manner. But until the source of the benzhydrol can be determined, meaningful analysis of the data is impossible.

The glpc data in Table 5 demonstrate that the increase in side product roughly parallels the increase in addition product. This is of importance in connection with the determination of A_c, the product corrected absorbance used to calculate the values shown in Figures 2 and 3. It was assumed that the only product formed was 1,1-diphenylethanol and therefore the extinction coefficient for this compound was used in determining the correction factors (20). The infinity readings indicate that the absorbance of the product mixture is reasonably approximated by this assumption. Also, because of the comparable rates at which the products increase, the correction should be valid throughout the reaction.

Very recently (29) benzopinacol was detected in the methylmagnesium bromide-benzophenone system and was reported in conjunction with the discovery that the reaction solutions contain free radicals as indicated by esr signals. The evidence for ketyl-type radicals in solution from the reaction of Grignard compounds with ketones is mounting (29,30,31, 32) and these radicals are generally suggested to be the precursors for pinacol formation. One report is of particular interest (30) since it

shows that the concentration of free radicals increases as the Grignard to ketone ratio increases. This is precisely the behavior observed for the extent of side reaction (Table 4) which also increases as the Grignard to ketone ratio increases.

However, the situation remains highly confusing. It has been reported (16) that the reaction between methylmagnesium bromide and 2,4-dimethyl-4'-methylmercaptobenzophenone does not give reproducible data at 10^{-5} M ketone. Apparently this means that the pseudo-first-order rate constant shows a dependence on the initial ketone concentration. However, this dependence disappears at higher concentrations (10^{-3} to 10^{-4} M ketone) and no side reaction was reported (16). With the ketone 4-methylmercaptoacetophenone (29), a ketone dependence was found with crude but not with recrystallized methylmagnesium bromide. Although esr signals were found with these solutions (29), no side reaction was reported. With benzophenone, esr signals, side reaction and a ketone concentration dependent pseudo-first-order rate constant were all reported (29).

It is clear that pinacol formation has not received adequate attention since kinetic data based on the disappearance of ketone (16, 17,18,19,20,21,29) have been interpreted solely in terms of the addition reaction. Some investigators (16,21,29) demonstrate the simple first-order dependence in ketone by showing that the rate constant is unchanged at different ketone concentrations. Indeed, inspection of Figure 3 reveals that the variation of the rate constant decreases as the Grignard to ketone ratio decreases. This is the trend observed for the formation of side product (Table 4). However, even in the region where k_{obs} is constant, a considerable amount of side product is still being formed.

Therefore, as far as the influence of the formation of pinacol is concerned, the behavior of the rate constant with ketone concentration appears to be an unreliable measure of the simplicity of the reaction. Until these matters are resolved, the conclusions presented in all of the previous studies must be viewed with caution.

CHAPTER IV

CONCLUSIONS

The reaction of methylmagnesium bromide with benzophenone in diethyl ether results in the formation of not only the addition product (1,1-diphenylethanol) but also a significant quantity of side products, one of which has been tentatively identified as benzopinacol. These results cast doubt on all of the mechanisms proposed thus far for the addition reaction because the contribution by the side reaction to the disappearance of ketone has not received adequate consideration. Unfortunately, the side reaction caused such analytical difficulties that no conclusions about the mechanism of the addition reaction could be reached.

CHAPTER V

RECOMMENDATIONS

A few suggestions for further work can be advanced at this point.

1. Analysis of benzopinacol may be facilitated by the use of silanized glass columns packed with an inert silanized support such as Gaschrom Q or Diataport S coated with 5% Ucon Polar 50HB5100.

2. If the analytical difficulties can be overcome, the order of the reaction in Grignard could be established by running reactions with benzophenone in large excess.

3. Once again, if the analytical difficulties can be surmounted, data on the reaction where Grignard and ketone are in comparable concentration would help to more clearly define the reaction mechanism.

4. It would be of interest to examine the possibility of shifting the equilibrium between free reactants and complex. Examination of Equation 6 reveals that if the equilibrium constant can be made very small by using a ketone with an electron-withdrawing group, then K[G] may be small enough so that the reaction will be third-order overall. With an electron-donating group, K[G] may be large enough so that the reaction will be second-order overall.

5. It may be possible to distinguish between a medium effect

and attack on the ketone by dimeric Grignard (Equation 5) as suggested by Smith and Su (16) for the reaction of methylmagnesium bromide at higher concentrations. In Part II of this thesis, it was shown that alkylmagnesium chlorides are dimeric in diethyl ether even at low concentrations. Therefore, reaction of methylmagnesium chloride with benzophenone in dilute diethyl ether solutions where medium effects are negligible might reasonably be expected to proceed by the dimer mechanism.

APPENDIX

Table 1. Reaction of 8.38×10^{-3} M Methylmagnesium Bromide with Benzophenone in Diethyl Ether at 25°C

$K_o = 2.50 \times 10^{-5}$ M*			$K_o = 3.71 \times 10^{-5}$ M*		
Time (sec)	A**	A_c***	Time (sec)	A**	A_c***
0	-----	0.450*	0	-----	0.668*
24	0.310	0.307	28	0.471	0.467
47	0.228	0.223	50	0.377	0.370
69	0.169	0.163	73	0.273	0.264
92	0.123	0.116	96	0.213	0.203
114	0.082	0.074	118	0.163	0.152
136	0.069	0.061	140	0.126	0.114
158	0.049	0.040	163	0.102	0.089
181	0.041	0.032	186	0.074	0.061
$K_o = 4.78 \times 10^{-5}$ M*			$K_o = 9.72 \times 10^{-5}$ M*		
Time (sec)	A**	A_c***	Time (sec)	A**	A_c***
0	-----	0.860*	0	-----	1.750*
24	0.770	0.767	25	1.558	1.550
44	0.563	0.555	48	1.165	1.150
68	0.409	0.398	71	0.894	0.873
91	0.301	0.288	94	0.721	0.697
111	0.249	0.234	116	0.577	0.550
133	0.201	0.185	141	0.457	0.427
155	0.158	0.142	164	0.372	0.340
177	0.131	0.114	188	0.301	0.268

*Extrapolated value for the initial benzophenone concentration.

**Uncorrected absorbance at 251 mμ.

***Product corrected absorbance at 251 mμ.

Table 2. Reaction of 6.45×10^{-3} M Methylmagnesium Bromide with Benzophenone in Diethyl Ether at 25°C.

$K_o = 2.90 \times 10^{-5}$ M*			$K_o = 4.70 \times 10^{-5}$ M*		
Time (sec)	A**	A_c***	Time (sec)	A**	A_c***
0	-----	0.522*	0	-----	0.845*
22	0.451	0.451	24	0.719	0.720
43	0.346	0.344	45	0.576	0.574
65	0.281	0.278	66	0.474	0.469
89	0.213	0.208	88	0.396	0.390
109	0.180	0.174	109	0.332	0.325
129	0.147	0.140	131	0.275	0.266
150	0.127	0.120	152	0.232	0.222
170	0.104	0.097	175	0.201	0.191
$K_o = 5.95 \times 10^{-5}$ M*			$K_o = 12.00 \times 10^{-5}$ M*		
Time (sec)	A**	A_c***	Time (sec)	A**	A_c***
0	-----	1.070*	0	-----	2.160*
22	0.938	0.938	28	1.770	1.770
42	0.770	0.766	50	1.435	1.425
64	0.629	0.623	75	1.129	1.115
85	0.517	0.508	99	0.948	0.930
107	0.432	0.422	123	0.785	0.762
127	0.374	0.362	148	0.642	0.616
148	0.312	0.299	175	0.536	0.509
169	0.264	0.250	200	0.449	0.419

*Extrapolated value for the initial benzophenone concentration.

**Uncorrected absorbance at 251 mμ.

***Product corrected absorbance at 251 mμ.

Table 3. Rate Constants for the Reaction of Methylmagnesium Bromide with Benzophenone in Diethyl Ether at 25°C

$G_o = 8.38 \times 10^{-3}$ M*		$G_o = 6.45 \times 10^{-3}$ M*	
$K_o \times 10^5$ M**	$k_{obs} \times 10^3 (sec^{-1})$***	$K_o \times 10^5$ M**	$k_{obs} \times 10^3 (sec^{-1})$***
2.50	14.7	2.90	9.50
3.71	12.4	4.70	8.56
4.78	11.5	5.95	8.66
9.72	9.90	12.00	8.25

*Initial methylmagnesium bromide concentration.

**Extrapolated value for the initial benzophenone concentration.

***Calculated from the slope of the line obtained by plotting time (sec) versus log A_c. It was assumed that the later points best represented the first-order disappearance of benzophenone as shown in Figure 1.

Table 4. Product Analysis of the Reaction Solutions

$K_o \times 10^5$ M**	$G_o:K_o$	Benzophenone (%)	Benzhydrol (%)	Unknown (%)	1,1-Diphenylethanol (%)
$G_o = 6.45 \times 10^{-3}$ M*					
12.00	54:1	10.4	7.5	1.4	80.7
5.95	108:1	4.1	13.2	1.6	81.2
4.70	137:1	4.5	16.2	2.0	77.3
2.90	222:1	5.3	22.2	0.7	71.9
$G_o = 8.38 \times 10^{-3}$ M*					
$K_o \times 10^5$ M**	$G_o:K_o$	Benzophenone (%)	Benzhydrol (%)	Unknown (%)	1,1-Diphenylethanol (%)
9.72	86:1	4.8	8.5	---***	86.7
4.78	176:1	6.3	16.0	---	77.7
3.71	226:1	7.1	17.7	---	75.2
2.50	336:1	7.4	20.4	---	72.2

*Initial methylmagnesium bromide concentration.

**Extrapolated value for the initial benzophenone concentration.

***Product not measured.

Table 5. Product Formation with Time From the Reaction of 6.45×10^{-3} M Methylmagnesium Bromide with 12.0×10^{-5} M Benzophenone in Diethyl Ether at 25°C.

Time (sec)	Benzophenone (%)	Benzhydrol (%)	1,1-Diphenylethanol (%)	$\frac{\text{1,1-Diphenylethanol}}{\text{Benzhydrol}}$
28	76.8	3.0	20.2	6.7
50	64.2	3.8	32.0	8.4
75	53.1	4.2	42.7	10.2
99	43.2	5.6	51.2	9.2
123	36.4	6.1	57.5	9.4
148	31.7	7.2	61.1	8.5
175	30.8	7.2	62.0	8.6
225	24.2	7.8	68.0	8.7
248	23.2	7.6	69.2	9.1

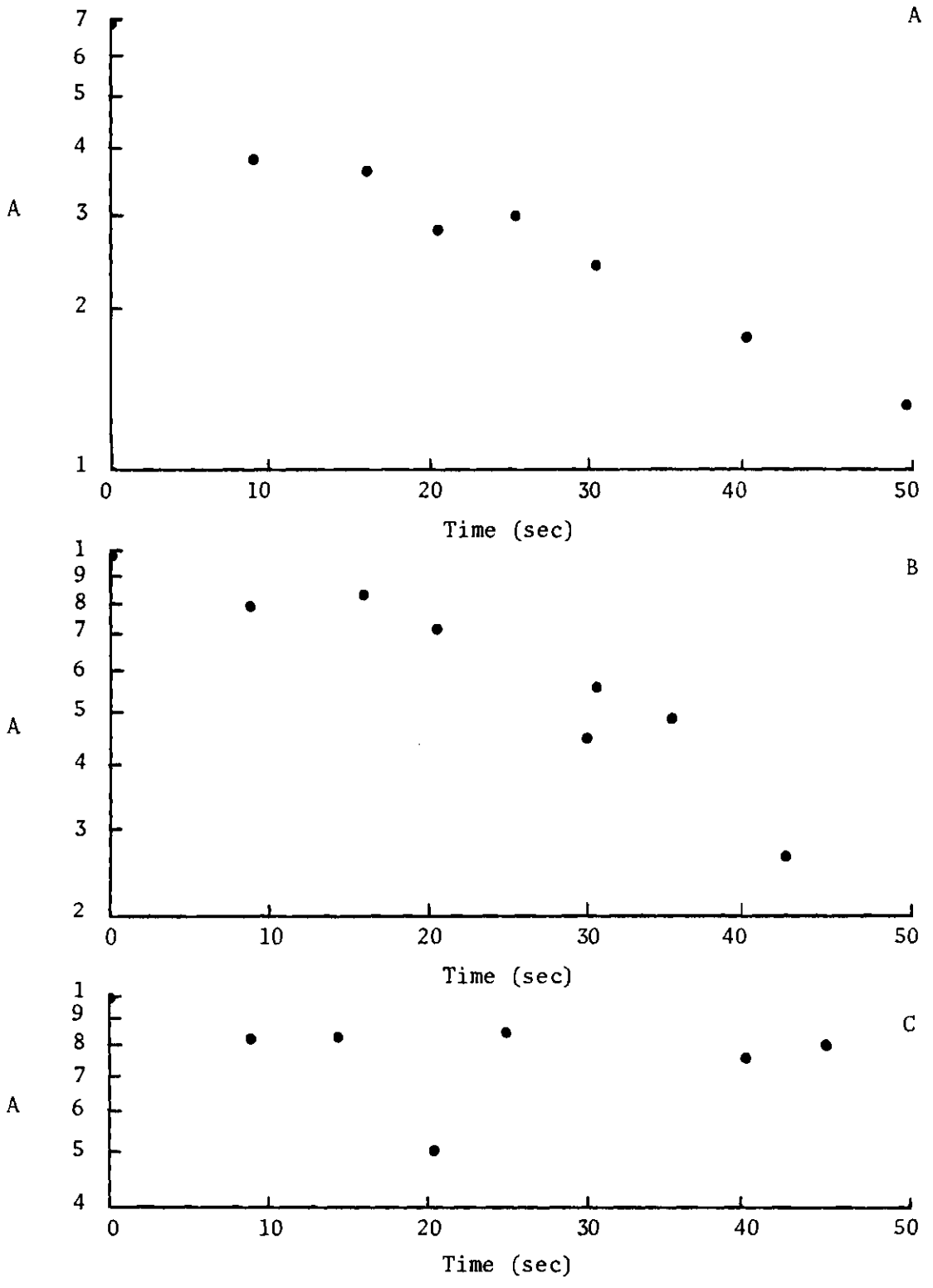

Figure 1. Effect of Preliminary Treatment of the Reaction Flasks on Disappearance of Benzophenone.

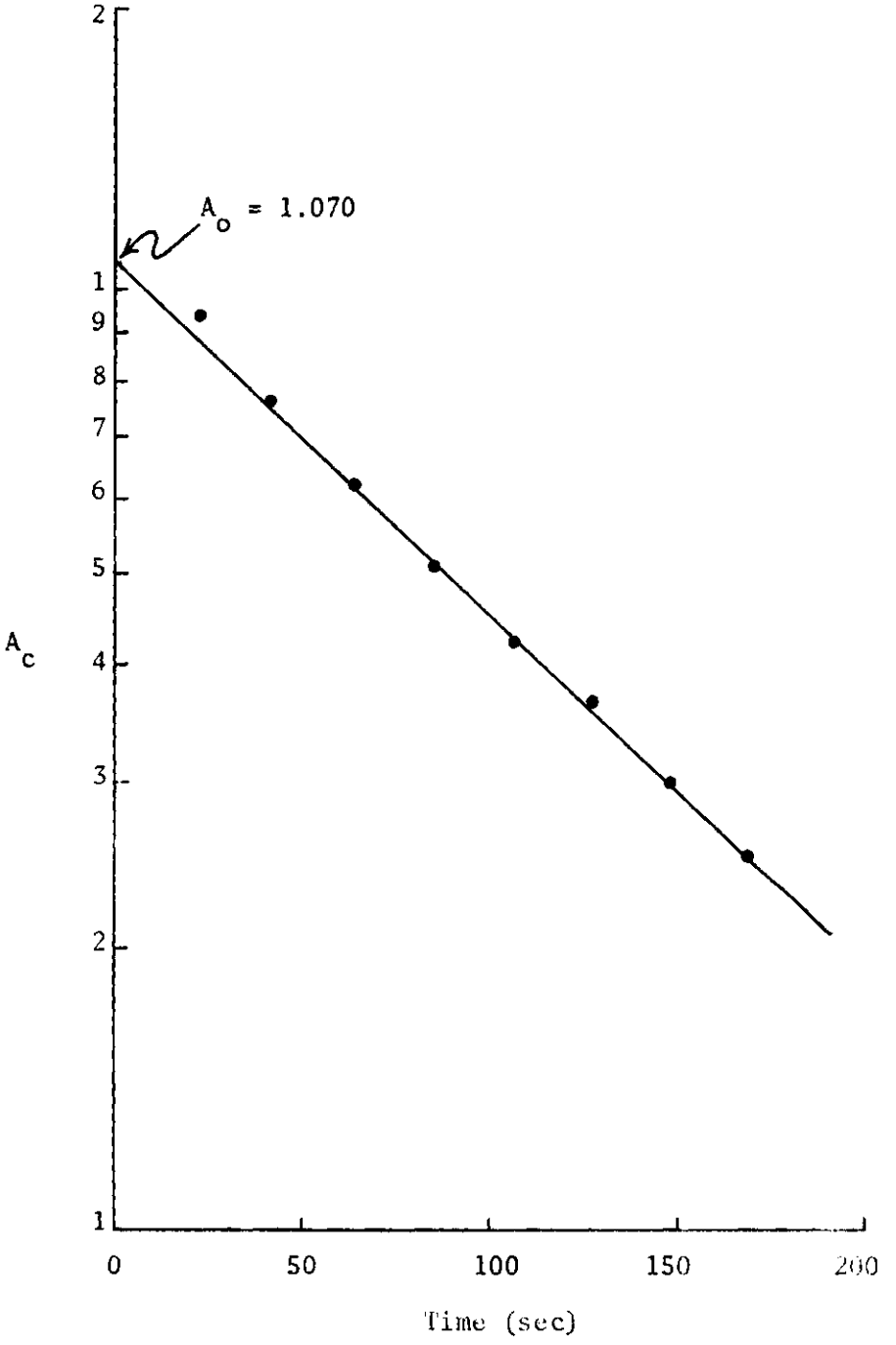

Figure 2. Calculation of Pseudo-First-Order Rate Constants. Determination of the Initial Absorbance, A_o.

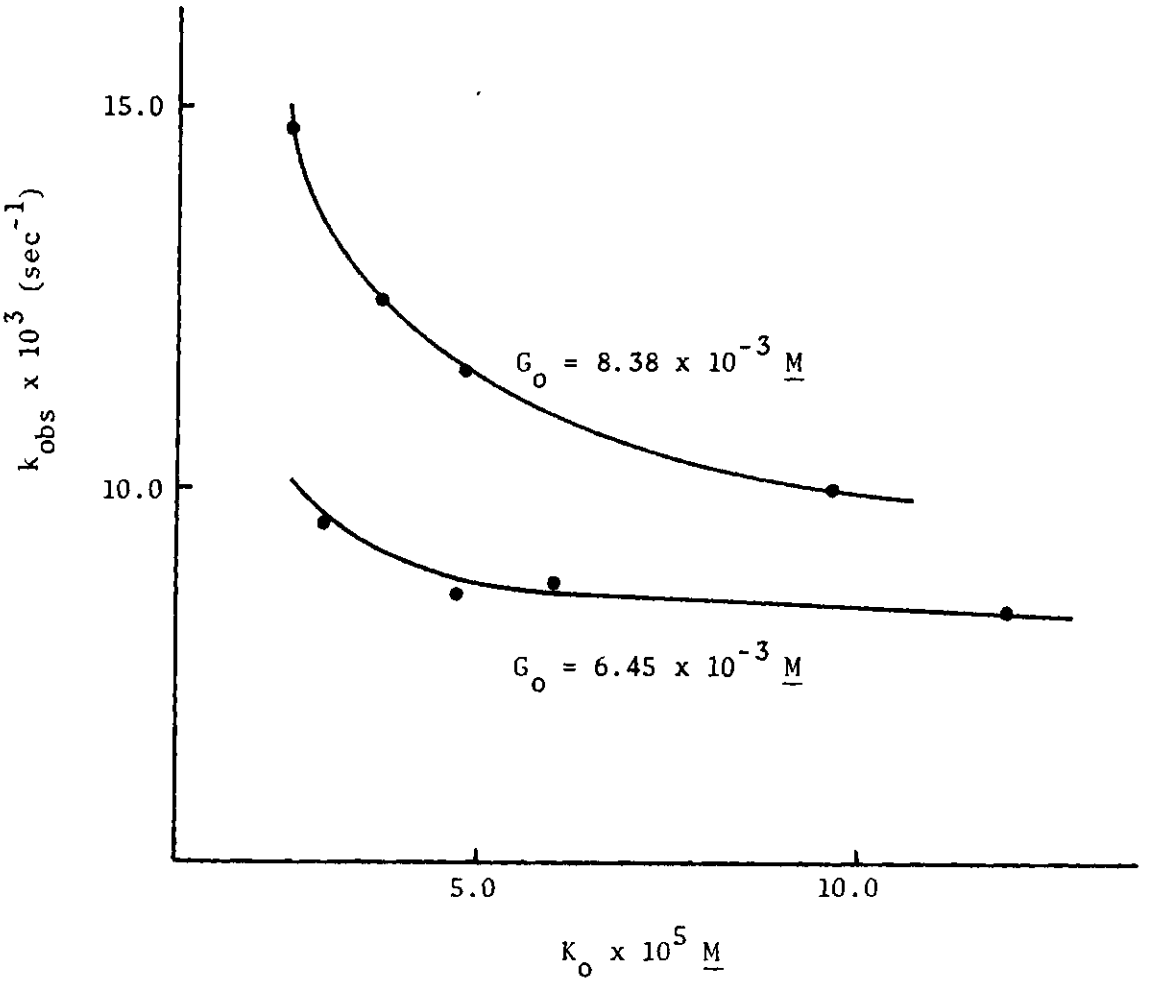

Figure 3. Variation of the Pseudo-First-Order Rate Constant (k_{obs}) with Initial Ketone Concentration (K_o).

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VITA

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His undergraduate work was done at Ohio University, Athens, Ohio, where he received a Bachelor of Science degree in chemistry in 1962. He remained at Ohio University for two additional years to obtain a Master of Science degree in chemistry in 1964 while working under the direction of Dr. R. K. Ingham.

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